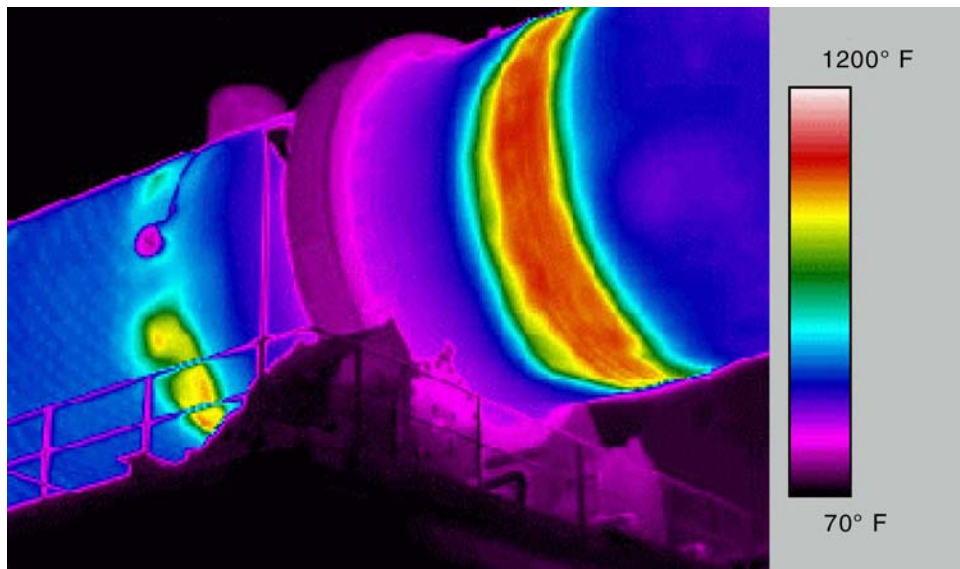


Energy and Emission Reduction Opportunities for the Cement Industry



Prepared for:

Industrial Technologies Program



U.S. Department of Energy

Energy Efficiency and Renewable Energy

Energy and Emission Reduction Opportunities for the Cement Industry

Prepared by:
William T. Choate

BCS, Incorporated
5550 Sterrett Place, Suite 306
Columbia, MD 21044



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Cover: Rotary kilns represent the largest energy consumer and carbon dioxide emission source of the cement/concrete industry. The cover diagram shows a thermal image of an operating kiln. The high temperature of the kiln surface (300°F to 400°F) accounts for about a 5% energy efficiency loss. The diagram on the cover depicts a kiln that has lost insulating refractory material and shows hot spots and a hot ring that will require future repair.

Acknowledgments

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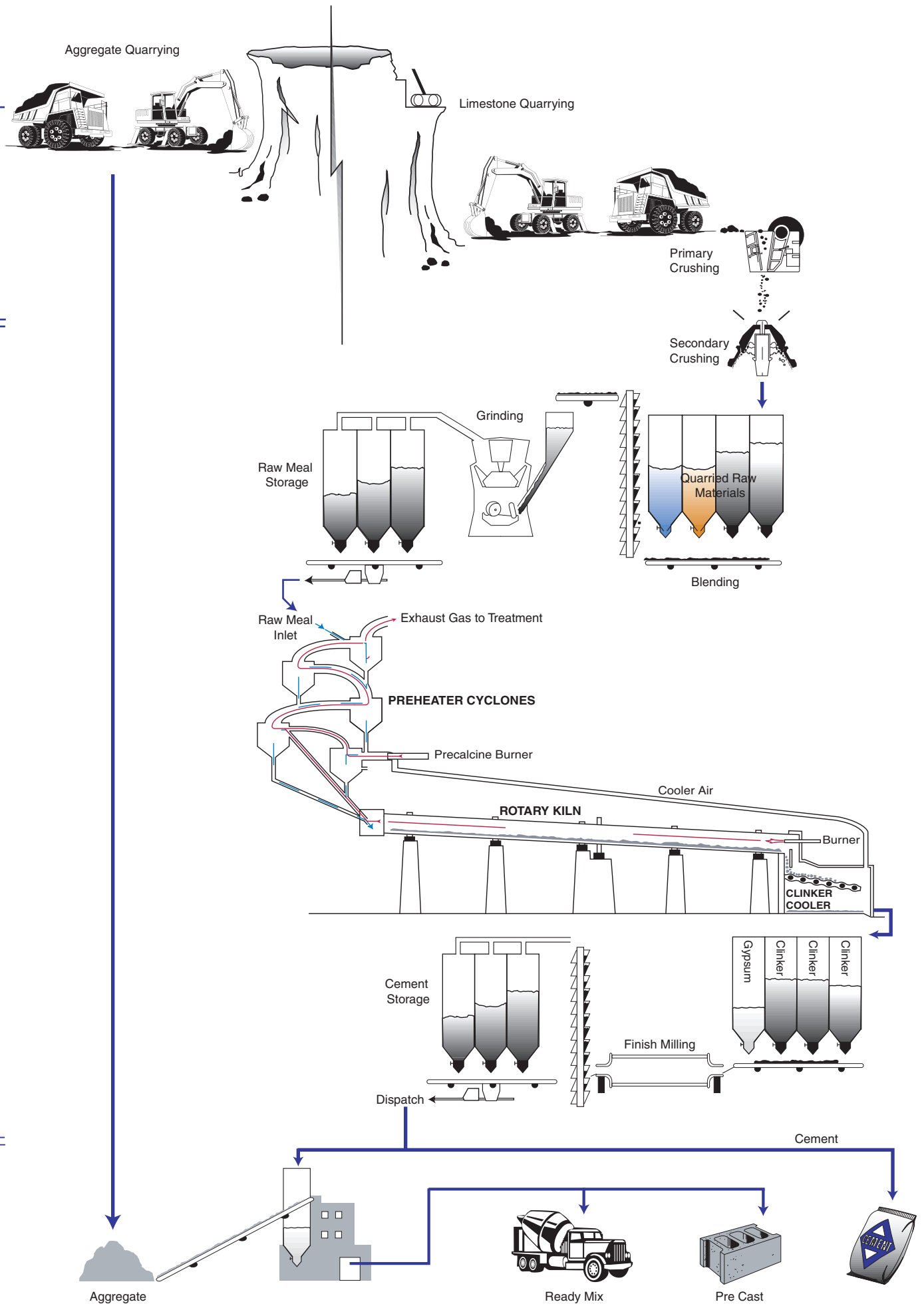
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QUARRYING

CEMENT MANUFACTURING

CONCRETE

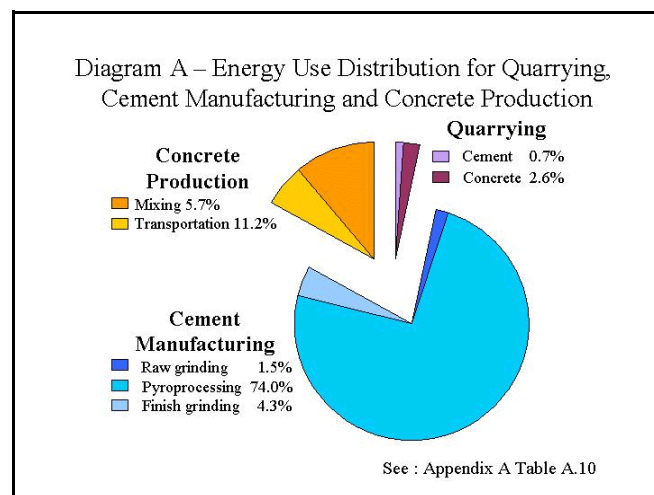


Executive Summary

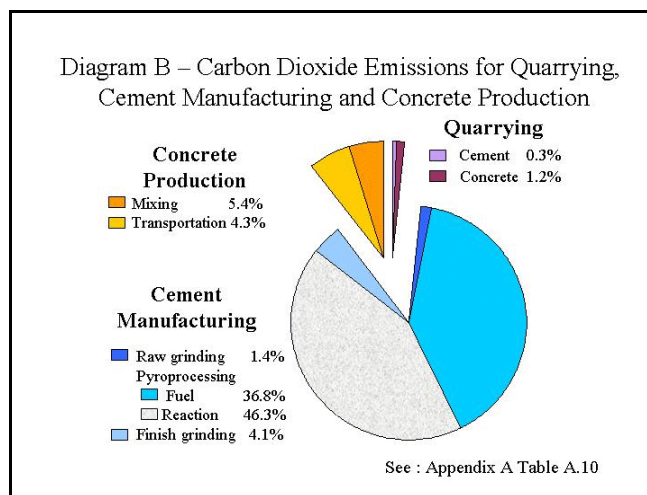
Cement is a gray, finely ground combination of minerals which, when mixed with water, sand, gravel, and other materials forms **concrete**. Cement provides the chemical bonds that hold the other materials together to form a dense rocklike substance. Concrete is the world's most commonly used construction material and second only to water as the most-consumed substance on Earth. Demand for cement is directly tied to the use of concrete in building construction and public works projects. It closely follows GDP growth in the United States and in developing countries. Nearly all cement is used to produce concrete. Cement manufacturing and concrete production are bound together in the Life Cycle Analysis of energy use and emissions of these industries.

The United States has 118 cement manufacturing facilities operating 192 kilns. These plants manufactured over 88,900,000 tonnes of cement in the year 2001. On average, they required 4,982,000 Btu to produce one metric ton (tonne) of cement, not including the energy required for quarrying raw materials. The production of concrete consumes nearly all manufactured cement. *Ready Mixed Concrete* is produced in more than 2,700 plants and accounts for over 75% of all concrete production. Over 390,646,000 cubic yards (687,000,000 tonnes) of ready mixed concrete were produced in 2002. Concrete blocks and precast products account for 13%, on-site concrete mixing accounts for 6%, and the remaining 6% of concrete production is used in well lining, mining operations, and other activities. Concrete accounts for about 20% of the energy and 12% of the CO₂ emissions associated with cement/concrete.

The cement/concrete industry operates at less than 40% thermal efficiency. This low efficiency suggests that there are significant opportunities to improve energy efficiency and reduce emissions. Diagram A shows the proportion of the more than 550×10^{12} Btu (0.55 quad) that were consumed in 2000 for U.S. quarrying, cement manufacturing, and concrete production. Cement manufacturing requires very high temperatures, 2,700°F (1,500°C), to initiate the reactions and phase changes necessary to form the complex mineral compounds that give cement its unique properties. Pyroprocessing in large rotary kilns is the operational step that provides the energy and environmental conditions necessary for the reactions and phase changes. This operation dominates the energy consumption and environmental impacts associated with the manufacture of cement and use of concrete and accounts for 74.2% of the industries' energy consumption. U.S. pyroprocessing systems, on average, operate at roughly 34% energy efficiency.



More than 104×10^6 tonnes of CO₂ emissions were associated with U.S. quarrying, cement manufacturing and concrete production. Diagram B shows the proportion by source of these emissions. The raw materials used in cement manufacturing undergo chemical reactions during pyroprocessing that result in the generation of carbon dioxide (CO₂). These chemical reactions produce 0.54 tonnes of CO₂ per tonne of cement, about 48×10^6 tonnes annually. Nearly 60% of the 68.9×10^6 tonnes of CO₂ produced annually in the United States from non-combustion industrial sources (chemical reactions) originate from cement manufacturing.¹ Industrial non-combustion CO₂ sources account for approximately 1.2% of all U.S. CO₂ emissions. In addition, the fuels burned to supply the energy necessary for pyroprocessing produce roughly 0.43 tonnes of CO₂ per tonne of cement. In total, pyroprocessing generates nearly 0.97 tonnes of CO₂ for each tonne of cement produced (86×10^6 tonnes annually) and accounts for 81% of the CO₂ emissions associated with the use of cement/concrete. The CO₂ produced from the chemical reactions is not influenced by changes in technology, equipment, or pyroprocessing energy efficiency. A consequence of the large portion of CO₂ generated from chemical reactions is that a 25% reduction in pyroprocessing energy use results in only an 11% reduction of total CO₂ emissions.



The greatest gains in reducing energy consumption and lowering emissions in the cement/concrete industry will be obtained with improvements in pyroprocessing. *Process* improvement will come from better energy management, upgrading existing equipment, adopting new pyroprocessing technologies, and in the longer term, performing the research and development (R&D) necessary to develop new cement manufacturing processes. Pyroprocessing is ideally suited to utilizing biomass and other non-traditional alternative fuel sources. Its extremely high operating temperature and long residence time ensure complete combustion of these fuel sources. Biomass fuels are considered to provide energy with near net-zero carbon-based emissions. R&D directed at developing the systems necessary to prepare and feed biomass fuels into pyroprocessing equipment will dramatically lower carbon-based emissions. Many industrial, manufacturing and consumer wastes are suitable alternate fuels for pyroprocessing (e.g., used oils, solvents, tires, and other wastes). R&D directed at safely increasing the use of alternate fuels provides an indirect means of improving energy efficiency. Alternate fuels are frequently assumed to have no energy requirement for their manufacture and their feedstock energy (energy inherent to the material) is normally associated with the finished product not the used product. Hence, when alternate fuels that are typically disposed of in landfills are utilized as fuels they provide a source of “free” energy.

Energy efficiency improvements and emission reductions can also result from changes in

the *Product Formulation* of cement. Research has shown that modifications to the cement formula are possible without a loss in desired properties or performance. These modifications include the addition of cement-like (pozzolanic) materials (e.g., fly ash, furnace slag, or other materials) that do not require the large energy inputs associated with pyroprocessing. Changes to cement product formulations require significant time to be incorporated into ASTM standards and be accepted in the marketplace. Concrete producers specify cement based on ASTM standards in order to guarantee the performance characteristics of concrete. Changes to these formulations are perceived as “risky” because change represents a move away from standards that have a very long and well-documented performance history. There is a trend in public works projects of specifying newer “low-energy” product formulations.

This report describes the cement industry and its technology. It provides background information necessary to develop realistic work plans to reduce energy usage and to lower CO₂ emissions. This report finds that opportunities exist both in the near-term and in the long-term for reducing energy usage and lowering emissions. Immediate and near-term improvements can be achieved by implementing demand-side energy management measures to improve energy efficiency and reduce electricity and fuel use. These improvements can come from utilizing free and low-cost options that include: motor, compressed air and process heater optimization software tools; participating in local and regional energy management training, workshops, and seminars; and conducting university-based energy assessments. Other site-specific near-term energy and environmental improvements can be achieved with contracted formal energy audits. Changes in product formulation also offer significant near-term energy and environmental improvements. Longer-term improvements could come from advanced research and development programs. However the cement industry, like most of the commodity materials industries, does not have the resources or incentives to conduct advanced and significant R&D on their own. Successful research and development programs will require significant collaboration between industry, government, and academia.

Introduction

Cement is a gray, finely ground combination of minerals which, when mixed with water, sand, gravel, and other materials forms **concrete**. Cement provides the chemical bond that holds the other materials together. Concrete, when newly mixed, is plastic and malleable, which allows it to be cast into shapes to build homes, sidewalks, superhighways, dams, skyscrapers and many other objects. Concrete is inert, nontoxic, naturally waterproof, and fire resistant. It is the world's most commonly used construction material.

The words cement and concrete in every day usage are frequently interchanged, even though cement is only one of the multiple materials used in the making of concrete (Is it a cement sidewalk or a concrete sidewalk?). Cement manufacturing and concrete production are bound together in any analysis of energy use and emissions.

The raw materials used to produce cement are primarily limestone, clay, shale, and silica sand (Appendix A Table A.3). These materials are quarried, crushed, and, for economy, are usually transported to a nearby cement plant. The cement plant proportions the raw materials to the correct chemical composition and grinds the material to a fine consistency. Small quantities of iron ore, alumina, and other minerals may be added to adjust the raw material mixture. The finely ground raw material, "raw meal," is fed into large rotary kilns, cylindrical furnaces 10 to 25 feet in diameter and 200 to 1,000 feet in length. The rotary cement kiln is the world's largest moving manufacturing machine and one of the hottest. It is typically set on a slight incline and rotates from 1 to 4 revolutions per minute. A large kiln may "pyroprocess" more than 300 tonnes of raw meal an hour. The raw meal is heated in the kiln to extremely high temperatures, about 1,500°C (2,700°F). The high temperature pyroprocessing causes the raw meal to react and form complex mineral compounds. These compounds exit the kiln as a hard nodular material called "**clinker**." Many newer cement plants use the hot exiting kiln gases to preheat the raw meal. Clinker is cooled and ground with approximately 5% gypsum (which controls concrete setting time) and other minor additives to produce cement.

Concrete is produced by blending cement with fine aggregate (sand), coarse aggregate (gravel or crushed stone), and frequently with small amounts of chemicals, called "admixtures." Admixtures are used to accelerate or retard setting time, control early plasticity properties, increase strength, improve resistance to acid and sulfates, control shrinkage, and improve freeze/thaw cracking. When water is added to the concrete mix at the job site, it forms a slurry that coats the surfaces of the aggregate and fills the voids to form rock-solid concrete. The process of hardening or setting is the result of the water hydration chemical reaction of the cement. The properties of concrete are determined by the exact chemical composition of cement

Concrete is second only to water as the most consumed substance on Earth, with almost one ton of it being used for each human every year. - Lafarge Coppee SA. Globe and Mail, October 20, 2000

Annual global production of concrete hovers around 5 billion cubic yards. Twice as much concrete is used in construction around the world than the total of all other building materials including wood, steel, plastic and aluminum. - Cement Association of Canada.

used, the additives, and the overall proportions of cement, aggregate, and water. Concrete contains about 12 weight percent cement. Because of the relatively small cement content, concrete is not energy intensive when compared to other construction materials.²

ENERGY AND EMISSION METRICS

Technologies, practices, and product use determine the energy consumption and environmental impact of a product. The energy values and emissions studied and presented in this report are based on a “value chain” analysis of the cement/concrete industry. Value chain analysis allows for the capture of the direct energy and feedstock inputs of each processing step (link) to build a cumulative value along the chain. A value chain analysis is an integral part of a Life Cycle Assessment (LCA) and provides valuable information and data values for organizations performing a complete LCA. LCAs are important to ensure that process improvements in one area are not merely shifting the energy and environmental burdens to another area. Numerous LCAs and energy inventories have examined the cement/concrete industry.³ These are valuable references.

On-site energy values are based on actual process measurements taken within a facility. These measurements are valuable because the on-site values are the benchmarks that industry uses to compare performance between processes, facilities, and companies. On-site measurements, however, do not account for the complete energy and environmental impact of manufacturing a product. A full accounting of the impact of manufacturing must include the energy used to produce the electricity, the fuels, and the raw materials used on-site. These “secondary” or “tacit” additions are very important from a regional, national, and global energy and environment perspective.

The “tacit energy” associated with the production and transportation of fossil fuels used for combustion adds roughly 3% to the energy values of the fuels. Tacit electrical energy and environmental impact measurements account for the fact that substantial electrical generation inefficiencies and transmission losses occur outside the cement manufacturing facility. It can take as much as three units of hydrocarbon or coal calorific energy to produce one unit of electric energy. Saving 1 kilo watt hour (kWh) of on-site electricity is equivalent to saving over 3 kWh of the energy contained in the petroleum or coal-based fuels used to generate electrical power. Typical U.S. grid electricity requires about 9,935 Btu of energy to deliver 1 kWh of on-site electricity (3,412 Btu) for use (Appendix A Table A.16). Industrial tacit energy values also account for feedstock energy. Feedstock energy is defined as the energy inherent in fuels that are used in the manufacturing as materials rather than fuels. The feedstock energy associated with cement and concrete production is near-zero. This report, for clarity, distinguishes between on-site energy values and tacit energy values with the use of a superscript (*Any value that is a tacit*

Concrete's *Relative Energy Intensity*²

Extruded Aluminum	184
Plastics	92
Structural Ceramics	17
Steel	12
Cement	8
Glass	7
Concrete	1

e.g., It requires 184 times more energy per unit mass to build with extruded aluminum compared to concrete.

value is denoted with the superscript “t,” e.g., 1.0^t kWh).

OVERALL ENERGY USE AND EMISSIONS

The annual cement/concrete energy “value chain analysis” from quarrying raw material to the final placement of concrete is shown in Table 1. The United States produced approximately 89,000,000 tonnes of cement in 2002. In total, the cement/concrete industry consumed over 550×10^{12} Btu (0.55 quad). Cement manufacturing is the most energy-intensive link, accounting for nearly 80%, 447×10^{12} Btu (0.447 quad) of the on-site energy consumed in the cement/concrete energy value chain.

The amount of energy required to produce one tonne of cement averaged 4,982,000 Btu/tonne of cement for U.S. plants (not including the energy required for quarrying the raw

Table 1 - Annual On-site Energy Use and CO ₂ Emissions Associated with Cement and Concrete Production				
	CEMENT		CONCRETE	
	Energy	CO ₂	Energy	CO ₂
	10 ⁹ Btu	10 ⁶ tonne	10 ⁹ Btu	10 ⁶ tonne
RAW MATERIALS: QUARRYING and CRUSHING				
Cement Materials	3,817	0.36		
Concrete Materials			14,287	1.28
CEMENT MANUFACTURING				
Raw Grinding	8,346	1.50		
Kiln: fuels	410,464	38.47		
reactions		48.35		
Finish Milling	24,057	4.32		
TOTAL CEMENT	446,683	93.00	446,683	93.00
CONCRETE PRODUCTION				
Blending, Mixing			31,444	5.65
Transportation			61,933	4.53
TOTAL			554,409	104.50

See: Appendix A Table A.10

materials). The most energy efficient U.S. plant required 3,230,000 Btu/tonne of cement while the least efficient used 8,150,000 Btu/tonne of cement.⁴ One unit operation, pyroprocessing accounts for 74.2% of the total on-site energy, more than 410×10^{12} Btu (0.41 quad), requiring nearly 4,617,000 Btu per tonne of cement for pyroprocessing alone.

The CO₂ emissions associated with the cement/concrete value chain are also presented in Table 1. Kilns and ancillary equipment used for pyroprocessing produce 83.1% of the CO₂ emissions. These emissions are generated by two mechanisms:

- ▶ Reaction-based CO₂ Generation – the thermochemical decomposition reaction or calcining of limestone ($\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$) and other minor raw materials produce CO₂
- ▶ Fuel-based CO₂ Generation – the combustion of fuels, used to obtain the high temperature needed for the calcining reactions, produce CO₂.

The calcium carbonate calcining reaction ($\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$) produces 0.785 tonnes of CO₂ per tonne of CaO. There is no technological or physical way to reduce calcination reaction emissions. Many cements contains about 61% CaO. Hence, the calcining reaction produces roughly 0.48 tonnes of CO₂ for each tonne of cement manufactured. This report calculated reaction CO₂ emissions to be 0.544 tonnes of CO₂ per tonne of cement based on the raw materials used by the U.S. cement industry (Appendix A Table A.11 and A.3). This difference can be accounted for by recognizing that the MgCO₂ portion of the raw materials also contributes to CO₂ emissions. Industrial emissions of CO₂ that are not caused by the combustion of fossil fuels, *Reaction-based CO₂ Generation*, accounted for 1.2% (68,900,000 metric tons of CO₂ equivalent)⁵ of total U.S. CO₂ emissions in 2000. The cement industry contributed 61% of this non-fuel value.⁵

The level of CO₂ emissions from fuels depends on the cement process and the fuels used. These emissions can be controlled to some degree by fuel selection, burner choice, burner controls, kiln operation, and heat recovery equipment. The fuel mix and operating systems that supplied the energy necessary to pyroprocess in U.S. cement kilns in 2001 produced roughly 0.433 tonnes of CO₂ per tonne of cement. In total, pyroprocessing generates nearly 0.977 tonnes of CO₂ for each tonne of cement produced (Appendix A Table A.11).

Cement manufacturing also generates other emissions of environmental concern. Particulates (dust) become airborne during the grinding, pyroprocessing, milling operations and with the conveying of raw materials and product within the cement plant. Large volumes of gases mixing with finely powdered material naturally result in airborne particulates. On-site airborne dust is captured and controlled through optimal design and application of electrostatic precipitators and bag-house filtration systems.⁶ These fine particulates can be difficult to capture and when they escape collection systems can spread over a large area.

Emissions of non-CO₂ gaseous pollutants are minimal because of the high temperatures and long residence times associated with kiln operations. Fuels and waste fuel materials are completely combusted and limestone in the raw meal acts as a natural "dry scrubber" that

captures many potential pollutants. Sulfur dioxide (SO_2) emissions from a cement manufacturing plant are dependent upon the sulfur content of the raw materials and fuels used. If a raw material or fuel with little or no sulfur content is used within a kiln, then there will be little or no SO_2 emissions. If there is a high sulfur content within the raw meal then the sulphide and organically combined sulphur will combust in the preheating stage, the majority of SO_2 formed is scrubbed out by the raw meal and only a small portion may be emitted to the atmosphere.⁷

Other emissions from fuel combustion include nitrogen oxides (NO_x) and carbon monoxide (CO). NO_x is produced during combustion due to the elevated temperatures in the kiln and to the presence of nitrogen in the air/fuel mixture. The temperatures at the firing end of the kiln approach $1,870^\circ\text{C}$ ($3,400^\circ\text{F}$). NO_x is produced in this environment due to the reaction of nitrogen in air with excess oxygen. The amount of NO_x produced is dependent upon the temperature and the amount of oxygen present. The higher the temperature or higher excess oxygen used in the kiln, the higher the resultant NO_x emissions will be. CO can result from poor solid-fuel feed systems in which sub-stoichiometric combustion will produce CO.⁸ However, the high temperature and long residence time associated with kiln operations provide little opportunity for CO emissions to occur.

The energy consumed for concrete production is associated mainly with three operations: quarrying fine and coarse aggregates; mixing and blending cement, aggregates, and admixtures; and transporting the concrete mix to the work site. The energy associated with concrete production is about 19.3% of the total energy associated with all quarrying, cement manufacturing, and concrete production.

CO_2 emissions associated with concrete production results from quarrying, blending, and transportation. Emissions from concrete account for 10.9% of the CO_2 emissions associated with both cement manufacturing and concrete production (Table 1). CO_2 emissions for concrete relative to energy input are smaller than for cement manufacturing, which produces CO_2 from both reaction chemistry and fuel use.

The U.S. Cement Industry

The U.S. Cement Industry produced 89,000,000 metric tons (tonnes) of building cement in 2002.⁹ The total value of cement plant sales was about \$8.6 billion.² U.S. cement industry plants directly employ about 16,400 workers. The United States ranks third in the world in overall cement output, behind China and India. Cement production worldwide is about 1,700,000,000 tonnes.¹⁰

Building cements accounts for about 95% of the cement sold in North America. This was used in the production of more than \$40 billion of concrete in the United States in 2001.² Masonry cement accounts for the remaining 5% of cement sales in the United States. Masonry cement is a combination of building cement and 30% to 50% limestone. It is used as mortar for blocks, bricks, stucco, and other building projects.

Cement manufacturing is a highly capital-intensive industry requiring large-scale equipment to be economically competitive. The capital investment per worker in the cement industry is among the highest in all industries. The high capital intensity limits the financial incentive to build new plants or update old plants. There are 118 cement facilities that operate 192 kilns in the United States (Diagram 1). Over 45% of U.S. kilns were built before 1980 and 5% of operating kilns were built prior to 1955.¹¹ The U.S. cement industry currently operates at an average 80% kiln utilization rate.¹²

The industry is diverse, involving 39 companies with no single company controlling more than 13.1% of the market based on tonnes produced. The five largest companies control nearly 50% of the market. Roughly 80% of the cement production capacity in the United States has foreign ownership or affiliation. Based on plant capacity, the top six countries with U.S. plant ownership are France (14.5%), Mexico (14.4%), Switzerland (14.3%), Germany (13.8%), Italy (9.6%), and Japan (5.4%). These countries each have two corporations present in the United States, except for Switzerland, which has only one. The top six

Table 2 - 2001 U.S. Cement Industry

Number of Companies	39
Number of Plants	118
Number of Kilns	192
Number of States with Plants	38
Largest Company Market Share (tonnes)	13.1%

Source: *U.S. Cement Industry Fact Sheet*, 2003 edition, Portland Cement Association

Diagram 1 - U.S. Kiln Locations



Source: Portland Cement Association

companies in terms of U.S. capacity are Holcim, Ltd. (Switzerland - 13.1%), Lafarge Coppee (France - 12.7%), CEMEX S.A. de C.V. (Mexico - 12.2%), Heidelberger Zement AG (Germany - 8.25%), Ash Grove Cement Co. (United States - 6.5%), and Buzzi UNICEM SpA (Italy - 4.4%).

The cement industry has reduced the amount of energy needed in cement production by more than 33% since the early 1970s (Appendix A, Table A.9). Cement manufacturers achieved greater energy efficiency by closing small plants and modernizing others. Energy savings were primarily achieved by shifting from the energy-intensive wet manufacturing process to the dry manufacturing process. Wet processing plants use water in raw meal grinding operations. This water must be evaporated in the pyroprocessing area. In 1974, 234 cement kilns used the wet process, currently only 54 wet process cement kilns are in operation. Cement plants have also reduced energy consumption and costs by taking advantage of excess heat from pyroprocessing to preheat the raw meal before it enters the kiln.

Pyroprocessing energy costs are significant and cement manufacturers attempt to utilize the lowest-cost energy supplies to reach the high temperatures required. Many cement plants routinely burn a mix of fuels in order to minimize energy costs. They are able to switch among a variety of conventional fuels and alternate waste fuels.

Table 3 shows the significant shift in fuel sources over the past thirty years. Cement manufacturers have switched from natural gas and petroleum based fuels to coal and petroleum coke for pyroprocessing. This switch was initially a result

of federal legislation in response to the "1973 Energy Crisis." The Energy Supply and Environmental Coordination Act of 1974 (ESECA, Public Law 93-319) compelled "Major Fuel Burning Installations" to stop burning natural gas and petroleum and to burn coal. The Powerplant and Industrial Fuel Use Act of 1978 (Public Law 95-620) required Congressional approval and a waiver from the Department of Energy for the use of fuels other than coal in heating plants over 50×10^6 Btu/hr. In 1987, Public Law 100-42 amended the Powerplant and

Table 3 - On-site Fuel Consumption for Cement Manufacturing (excluding Quarrying)

	1971		2000	
	Btu/tonne	Percent	Btu/tonne	Percent
CONVENTIONAL FUELS				
Coal	2,639,000	36%	2,984,100	60%
Petroleum Coke	39,600	1%	760,700	15%
Natural Gas	3,347,100	45%	261,600	5%
Middle Distillates	88,300	1%	39,400	1%
Residual Oil	808,900	11%	3,900	0%
Gasoline	7,400	0%	4,600	0%
LPG	1,400	0%	300	0%
ALTERNATE/WASTE FUELS				
Oils	0		15,000	0%
Solvents	0		251,900	5%
Tires	0		115,400	2%
Solids	0		12,600	0%
Misc.	0		7,600	0%
FUELS Subtotal	6,931,700	93%	4,457,100	90%
ELECTRICITY	488,600	7%	524,700	11%
TOTAL	7,420,400	100%	4,981,700	100%

Source: Cement Industry Fact Sheet 2002 edition
Portland Cement Association

Industrial Fuel Use Act to repeal prohibitions against the use of natural gas and petroleum. Fuel switching is costly in terms of capital costs and today's lower cost/Btu of coal compared to petroleum or natural gas economically favor coal as the fuel of choice.

The switch from petroleum and natural gas results in an increase in CO₂ fuel emissions per Btu consumed. Coal produces about 1.8 times more CO₂ than natural gas and about 1.2 times more than residual oils on a Btu basis. Overall the industry has lowered their CO₂ emission by 15% between 1971 and 2000. This was accomplished with improvements in energy efficiency that produced a reduction in the Btu/tonne requirement for production of cement by over 33%. If year 2000 plants were operating on the 1971 fuel mix, emissions would have been lowered by 21% (Appendix A Table A.9).

Kilns are ideally suited to recycling alternate/wastes for recovering their energy value because of the intense heat of pyroprocessing. The cement industry has steadily increased its use of waste materials to fuel cement kilns, and currently relies on the combustion of waste materials for 8.2% of its energy needs. Cement plants can burn many household and industrial wastes, including waste solvents, scrap tires, used motor oils, surplus printing inks, dry-cleaning solvents, paint thinners, petroleum sludge, and agricultural wastes such as almond shells and rice hulls.

Nearly all cement is used to produce concrete. *Ready Mixed Concrete*, concrete mixed at local plants for delivery in the familiar trucks with revolving tanks, accounts for over 75% of all concrete production. Concrete masonry (e.g., 8 x 16 inch blocks) and precast concrete products account for 13%, contractor (on-site concrete mixing) accounts for 6%, and the remaining 6% of concrete production is used in well lining, mining operations, and other activities.¹³ The United States has about 2,700 ready mixed concrete companies that operate 5,000 to 6,000 plants and utilize 70,000 to 80,000 trucks for delivery. Ready mixed companies employ between 126,000 and 144,000 workers. They supplied more than 390,646,000 cubic yards of concrete in 2002, enough to build a road ten feet wide, four inches thick that encircles the globe 51 times.¹⁴

Cement

Cement is the key ingredient in concrete products. Comprising roughly 12% of the average residential-grade ready mixed concrete, cement is the binding agent that holds sand and other aggregates together in a hard, rock-like mass. Building cement or portland cement accounts for about 95% of the cement produced in North America. Portland cement was patented in 1824 by Joseph Aspdin, an English stonemason, and named after a quarried stone it resembled from the Isle of Portland.

The properties of concrete depend on the quantities and qualities of its components. Because cement is the most active component of concrete and usually has the greatest unit cost, its selection and proper use are of paramount importance in obtaining the most economical balance of properties desired for any particular concrete mixture. Different types of portland cement are manufactured to meet different physical and chemical requirements for specific purposes, such as durability and high-early strength.

The American Society for Testing and Materials (ASTM) Specification C-150 provides for eight types of portland cement (Appendix B). ASTM standards serve as the basis for manufacturing, procurement, and regulatory activities. In 2001, more than 88% of the portland cement produced in the United States was ASTM Type I and II (or Type I/II); Type III accounted for about 3.5% and Type V accounted for 4.4% of cement production¹⁵. Air-entraining cements Type IA, IIA, and IIIA are available but have little market share. Concrete producers prefer to use admixture for air-entraining during concrete production, where they can have better control in obtaining the desired air content.

The chemical composition of cement is what distinguishes one type from another. Portland cements are made up of clinker and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). The four main compounds in clinker are: tricalcium silicate ($3\text{CaO} \cdot \text{SiO}_2$), dicalcium silicate ($2\text{CaO} \cdot \text{SiO}_2$), tricalcium aluminate ($3\text{CaO} \cdot \text{Al}_2\text{O}_3$), and tetra-calcium aluminoferrite ($4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$). The industry commonly uses an abbreviated notation differing from normal chemical formulae. These compounds are designated as C_3S , C_2S , C_3A , and C_4AF , where C stands for calcium oxide (CaO , lime), S for silica (SiO_2), A for alumina (Al_2O_3), and F for iron oxide (Fe_2O_3). The approximate composition of compounds in typical portland cement is listed in Table 4.

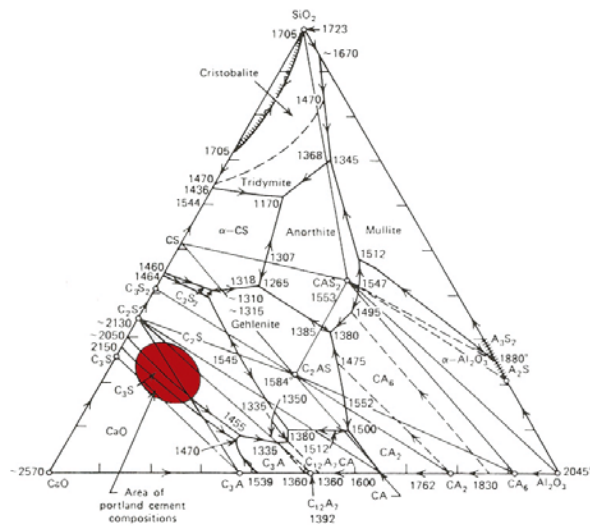
Table 4 - Final Composition of Typical Portland Cement

Cement Compound	Weight Percentage	Chemical Formula	Abbreviated Notation
Tricalcium silicate	50 %	Ca_3SiO_5 or $3\text{CaO} \cdot \text{SiO}_2$	C_3S
Dicalcium silicate	25 %	Ca_2SiO_4 or $2\text{CaO} \cdot \text{SiO}_2$	C_2S
Tricalcium aluminate	10 %	$\text{Ca}_3\text{Al}_2\text{O}_6$ or $3\text{CaO} \cdot \text{Al}_2\text{O}_3$	C_3A
Tetracalcium aluminoferrite	10 %	$\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$ or $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$	C_4AF
Gypsum	5 %	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	

The industry frequently reports the composition of cement as a percentage of the raw materials and not as a percentage of the final compounds formed. The composition of portland cement falls within the range of 60% to 67% lime (CaO), 19% to 25% silica (Si), 3% to 8% alumina (Al_2O_3), and 0.3% to 6% iron oxide together with 1% to 3% sulphur trioxide, derived mainly from the added gypsum, 0.5% to 5% magnesia, and 0.3% to 1.3% alkalies. Titanium oxide is usually present to the extent of 0.1% to 0.4%. Manganese oxide is usually present only in small amounts, except when blast-furnace slag is used as a raw material, then it may rise to 1%.

The proportions of components in the final composition results from obtaining a phase equilibrium of all components in the raw meal, ash from fuels, and from other additions. The final compounds reflect the effects of kiln temperatures, residence time, quenching, oxygen availability, and many other kiln conditions. The actual final components are complex chemical crystalline and amorphous structures. Diagram 2 is a phase diagram of the major raw meal pyroprocess products.¹⁶ About 20% to 30% of the raw materials become liquid at the highest temperatures in the kiln. Portland cement composition is noted in one small area. Complex reactions and phase changes occur at the surfaces of the solids and within the liquid. The behavior of each type of cement depends on the mixture of final components.

Diagram 2 - Phase Diagram of Major Cement Components¹⁴



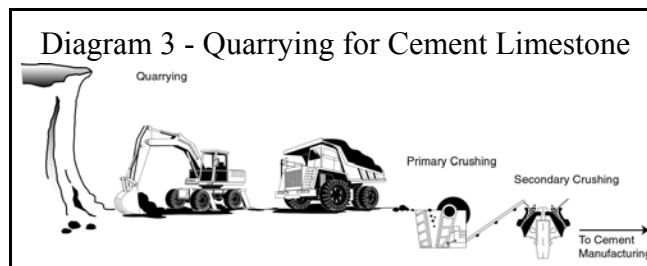
CEMENT MANUFACTURING PROCESS

Cement manufacturing requires exacting measurements and careful controls to produce a product that meets precise chemical and physical specifications. The first step in the cement manufacturing process is the quarrying of a combination of raw materials (Appendix A - Table A.3) that when sized, blended, and processed yield the exact chemical composition required. These raw materials then undergo a series of high temperature chemical reactions and physical changes after which they are ground into a very fine, carefully sized powder.

Quarrying

Generally, cement raw materials consisting of mainly limestone (71%) and combinations of cement rock (16%), shale, clay, sand, or iron ore are extracted from a quarry near the cement plant.

Limestone and cement rock are the most common source of CaCO_3 for cement production, making up about 87% of the raw materials (Appendix A - Table A3). Typically, the limestone used in cement production contains 75% to 90% CaCO_3 with the remainder predominately MgCO_3 and minor impurities. Limestone is typically categorized as high-calcium (<5% MgCO_3), magnesium-limestone (5% to 20% MgCO_3), or dolomitic-limestone (>20% to <45.6% MgCO_3). Cement rock is impure limestone possessing the ideal balance of silica, alumina, and CaCO_3 for portland cement¹⁷.



A typical limestone/cement rock quarrying process for producing crushed and broken stone includes:

- removal of the overburden (i.e., soil, clay, and loose rock overlaying the deposit)
- blasting of the limestone deposit
- loading and transporting the blasted limestone to the crushing plant
- Crushing to reduce stone to about 5 inches (125 mm) in primary crushers, then to roughly 3/8 inch to 3/4 inch (10 mm to 19 mm) in secondary crushers.

The total energy required to quarry and process limestone/cement rock is 29,932 Btu/tonne. The quarrying of the limestone/cement rock consumes approximately 88% of the total energy requirement and the crushing of the ore accounts for the remaining 12% of the energy requirement.¹⁸ Table 5 provides a detailed listing of the equipment used and the Btu per tonne consumed for each equipment operation.¹⁹ Appendix A Table A.5 lists quarrying fuels and consumption values. In the quarrying of the limestone/cement rock, diesel fuel is the main source of energy and provides about 80% of the quarrying operations energy. Diesel fuel is used to run the heavy machinery in the limestone quarry's daily operation. Utilization of biodiesel provides an opportunity for quarrying operations to lower lifecycle emission profiles.

Primary crushing reduces quarried stone to about 5 inches. Primary crushed stone is fed into secondary crushers where it is broken down to a size (~0.375 to ~0.75 inch) suitable for feed to the fine grinding machines located at the cement manufacturing plant. Crushing consumes an estimated 2,927 Btu/tonne of limestone.

Limestone/cement rock account for 87% of the raw materials used to produce cement. The energy and emissions associated with quarrying of the remaining 13% of raw materials has been estimated using the limestone/cement rock data (Appendix A Table A.6).

The environmental issues related to quarrying are mostly local and are common to most surface mines. These issues include dust, increased sediment loads to local streams, noise, and ground vibrations from blasting.

Raw Material Preparation

When raw materials arrive at the cement plant, they are stored in dry sheds or silos. These materials are then carefully proportioned accounting for combustion fuel ash and other additives to create a cement with a specific chemical composition. Two different methods, dry-process and wet-process, are used to grind raw materials. In the dry-process, raw materials are proportioned, ground to a powder, blended together and fed to the kiln in a dry state. In the wet-process, a slurry is formed by adding water to the properly proportioned raw materials. The grinding and blending operations are then completed with the materials in slurry form. This significantly lowers dust levels but requires additional energy to later remove the water from the raw meal.

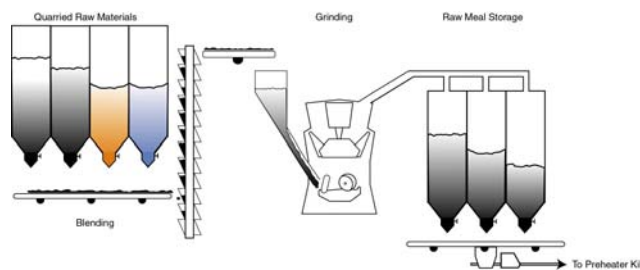
Limestone, ~0.375 inch to ~0.75 inch in size, is blended with other raw materials (Appendix A Table A.3) and fed into grinding mills where it is reduced in size until approximately 70% to 85% passes a 200-mesh screen (0.0027 inch, 0.069 mm screen opening). Raw meal grinding equipment

Table 5 - Energy Consumption for Surface Limestone Quarrying

On-site Operations	Btu/Tonne
QUARRYING	
Percussion Drill	6,140
Hydraulic Shovel	5,670
Rear-Dump Truck	4,030
Bulldozer	3,420
Pick-Up Trucks	2,250
Water Tanker	1,170
Service Truck	1,120
Lighting Plant	66
Front-End Loader	187
Bulk Truck	147
Pumps	2,250
Grader	7
subtotal	26,457
CRUSHING	
Conveyor	182
Screens	366
Primary Crushers	1,830
Secondary Crushers	1,097
subtotal	3,475
TOTAL	29,932

Source: U.S. Department of Energy, Mining Industry of the Future, *Energy and Environmental Profile of the U.S. Mining Industry*, pg. 9-9.

Diagram 4 - Raw Material Preparation



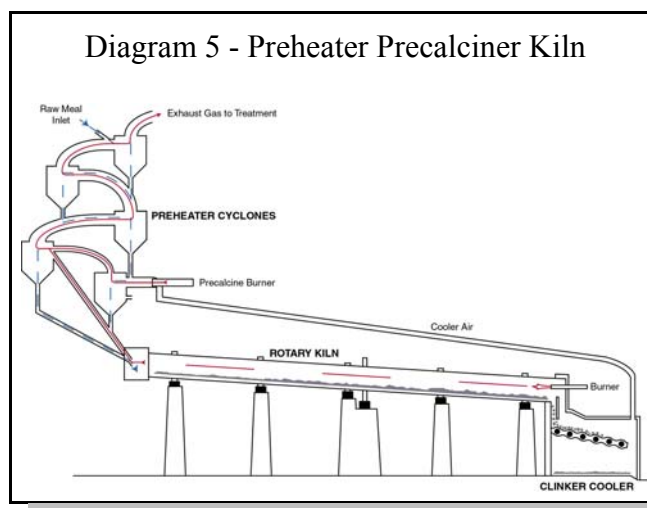
includes: ball mills, tube mills, compound mills, ring roll mills, and impact mills. Raw meal grinding has a significant effect on pyroprocessing and clinker quality. The raw meal quality (fineness, the amount and nature of oversized particles), and flowability (kiln circulating and separation patterns, and conductive energy transfer) affect the final clinker quality.

Raw material grinding consumes about 2% of the on-site energy associated with cement manufacturing. Grinding and milling are electrically driven processes. In addition to the electricity consumed on-site, electric processes have large tacit energy requirements associated with the generation and transmission of electricity. Grinding raw materials for cement manufacturing consumes approximately 93,885 (273,235¹) Btu/tonne of cement (Appendix A Table A.11). Grinding energy is a function of numerous factors including how the material fractures (under slow pressure, under impact), compressive strength, coefficient of elasticity, hardness, starting and finish size, desired particle distribution, etc. The exact amount of work required for grinding is difficult to calculate. Grinding efficiency ranges from 6% to 25% based on the thermal measurements.²⁰ Since grinding consumes electricity, a costly energy source, cement manufacturers work to improve grinding efficiency. On-site grinding efficiency improvements provide significant offsite energy savings related to electric generation and transmission losses.

Kiln Operations

Pyroprocessing in giant rotating furnaces or kilns represent the major technical process common to all cement plants. It is also the most technically complex and energy-intensive operation from quarrying to concrete placement. Rotary cement kilns are cylindrical, refractory-lined steel furnaces that range from 200 to more than 1,000 feet long and from 10 to over 25 feet in diameter. Cement kilns are the world's largest piece of moving industrial process equipment - and one of the hottest.

Blended raw material is fed into the upper end of the tilted rotating kiln. As the kiln slowly rotates (1 to 4 revolutions per minute), the raw material tumbles through progressively hotter zones toward the flame at the lower end of the kiln. The mixture passes at a rate controlled by the diameter and rotational speed of the kiln. The flame is fueled by powdered coal, petroleum coke, natural gas, oil, recycled materials, or other fuels. A 1870°C (3400°F) flame heats the mixture to 1480°C (2700°F). The extreme heat triggers a series of chemical reactions. The raw materials break down (calcine), become partially molten, and fuse together into nodules called "clinker."



The raw meal undergoes complex chemical and physical changes as it tumbles, then flows, through the kiln. These chemical reactions and changes can be viewed as a sequence of thermal events, some of which may occur outside the kiln in a preheater and/or precalciner section. The following describes the sequence of chemical and physical changes:

- Evaporation of uncombined water from raw material preparation in the wet process as material temperature increases to 100°C (212°F).
- Dehydration: the evolution of bound water from the material as temperatures increase from 100°C to approximately 550°C (1,020°F) to form the unhydrated oxides of silicon, aluminum, and iron.
- Calcination of the calcium carbonate (CaCO_3) to calcium oxide (CaO) and magnesium carbonate (MgCO_3) to magnesium oxide (MgO) with the evolution of carbon dioxide (CO_2) between 900°C (1,650°F) and 980°C (1,800°F). The CO_2 gas fluidizes the raw materials, which changes raw material movement from tumbling to flowing.
- Reaction of CaO with silica to form dicalcium silicate.
- Reaction of CaO with the aluminum and iron-bearing constituents to form the liquid molten phase.
- Formation of the clinker nodules. Reactions bonding the calcium oxide and silica oxide to form dicalcium and tricalcium silicates, and small amounts of tricalcium aluminate and tetracalcium aluminoferrite. These compounds form the four principal components that determine the properties of the cement manufactured.
- Evaporation of volatile constituents (e.g., sodium, potassium, chlorides, and sulfates).
- Reaction of excess CaO with dicalcium silicate to form tricalcium silicate.
- Formation of clinker as material approaches the exit of the kiln at temperatures of approximately 1,500°C (2,700°F).

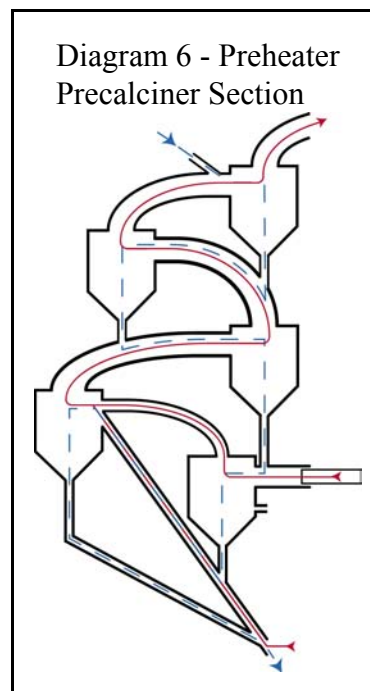
Clinker is discharged red-hot from the lower end of the kiln and transferred to various types of coolers to recover thermal energy and lower the clinker to handling temperatures. Clinker, when cooled, is typically gray, glass-hard, spherically shaped nodules that range from 0.3 to 5.0 centimeters (0.125 to 2.0 inches) in diameter.

Kilns are divided into two groups, dry-process (80.5% of U.S. capacity) and wet-process depending on how the raw materials were prepared. Wet-process kilns are fed raw material as a slurry with a moisture content of 30% to 40%. A wet-process kiln needs additional length to evaporate the water contained in the raw material feed. Nearly 33% additional kiln energy is consumed in evaporating the slurry water. Wet-process kilns tend to be older fully capitalized operations. The last wet-process kiln to be built in the United States was constructed in 1975.

Dry-process kilns are fed dry powder raw materials. Three major variations of dry-process kilns are in operation: no-preheater kiln, preheater kiln, and precalciner kiln. Dry-process kilns operate with high exiting gas temperatures. In most dry-process no-preheater

operations the kiln is equipped with metal chain sections at the gas exit end. These chains hang from the refractories in the gas path. The gases pass through the chains, which absorb heat from the gas stream. As the kiln rotates, the chains intermix and become covered by the feed raw materials at the bottom of the kiln. The chains transfer their thermal energy by conduction to the raw material entering the kiln.

Most dry process plants preheat the finely ground raw material before it enters the kiln. The preheating takes place typically in a tall tower consisting of multistage countercurrent-flow cyclones, Diagram 6. These towers can be over 450 feet tall. Multiple solid/gas cyclone heat exchangers swirl the raw materials with the hot exit gases from the kiln and heat them quickly and efficiently. Some preheater towers include a special preheater section which contains a fuel combustion chamber. These sections provide some of the precalciner energy and are referred to as precalciner.



Today, the most common type of cement kiln (accounting for 80% of capacity in the United States) is a dry-process kiln, in which the raw meal is processed dry. Many older kilns (20%) still in operation use the wet-process. Table 6 provides an inventory of U.S. cement kilns. Each kiln, wet-process and the three versions of dry-process, operate with a different energy efficiency. The theoretical energy requirement for pyroprocessing (i.e., the minimum energy required to remove hydrated water, calcine, and raise the temperature to obtain the phases necessary for cement clinker) is about 1,710,000 Btu/tonne of clinker.²¹ The thermal efficiencies for various kiln processes are also shown in Table 6. On average, pyroprocessing operations run at about 34% thermal efficiency. This leaves ample opportunities to improve thermal performance. The last chapter of this report, *Opportunities for Improving Energy Efficiency and Reducing CO₂ Emissions*, and in particular Table 9, examines the thermal balance of the kiln and kiln losses and suggests where efficiency improvement could have a major impact.

Table 6 - Approximate Energy Consumption in U.S. Kilns by Number and Process

	U.S. Kilns ¹	Percent of Kilns	2000 Clinker Production, tonnes	Percent of U.S. Capacity	Million Btu per tonne ³	Percent Thermal Efficiency
Total U.S. Kilns	192	100%	71,860,000 ²	100%	4.98	34%
Wet Process Kiln Plants	54	28.4%	14,030,000 ²	19.5%	6.25	27%
Dry Process Kiln Plants	136	71.6%	57,830,000 ²	80.5%	4.67	37%
No Preheater or Precalciner	59	31.1%	12,950,000 ²	18.0%	5.64	30%
Preheater (only)	35	18.4%	13,830,000 ²	19.2%	4.58	37%
Precalciner	42	22.1%	31,050,000 ²	43.2%	4.31	40%
Preheater/Precalciner ⁴	77	40.5%	44,880,000 ²	62.4%	4.39	39%

1 - Kiln process types were provided by the Portland Cement Association. Two kilns were not classified and are not listed as wet or dry process kilns. These data represent approximately 92% of U.S. clinker production and about 93% of U.S. kilns (Appendix A Table A.1).

2 - 2000 U.S. and Canadian Labor-Energy Input Survey, Portland Cement Association, pages 12-27

3 - 2000 U.S. and Canadian Labor-Energy Input Survey, Portland Cement Association, page 7

4 - Includes plants that are preheater only, precalciner only and combinations

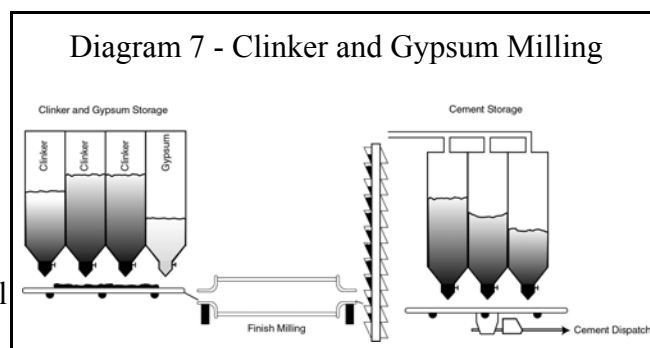
Clinker Cooling

Red-hot clinker tumbles from the kiln onto a grate and is cooled by recirculating air. The hot air recovered from this cooling process is recycled back to the kiln or preheater system to recover its thermal energy. After energy is recovered from the process gases, the gases are routed to pollution control devices. Electrostatic precipitators or fabric filters remove particulate matter (dust) from the gases before they are discharged to the atmosphere. Particulate removal efficiencies of 99.7 % are common throughout the industry.

Cement Milling

Cooled clinker is combined with approximately 3% to 6% gypsum and ground/milled into an extremely fine gray powder. This fine gray powder is cement. Gypsum is used to control the setting time of concrete.

Finish milling usually uses tube or ball mill equipment. Clinker is milled so finely



that nearly all of it passes through a 200 mesh (0.0027 inch, 0.069 mm) screen that will hold water. The final powder has a surface area of 3,000 to 5,000 cm²/g and about 85% to 95% of the powder will pass through a 325-mesh screen (0.0017 inch, 0.043 mm). The fineness of the cement is an important property and affects the rate of hydration. The finer the milled cement, the more surface area is available for hydration. The greater area for hydration causes greater early strength and more rapid generation of heat. Cements are classified by their fineness with Type III containing a more finely milled cement than Type I cement.

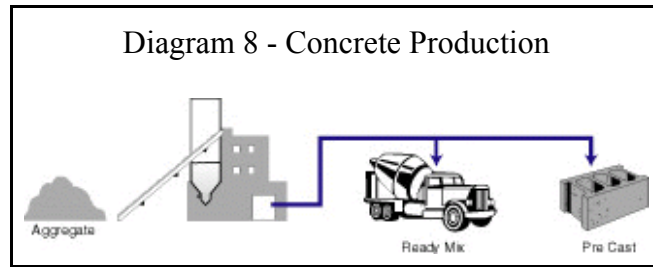
Clinker milling uses the same general type of equipment as raw meal grinding. However, the final product is much finer and requires almost three times the energy 270,610 (778,043^t) Btu/tonne of cement as raw meal grinding requires (Appendix A Table A.11). Clinker milling is not energy efficient and typical cement milling systems can consume nearly twenty times their theoretical energy requirement.²² After milling, portland cement is ready to be bagged or shipped in bulk by truck or rail to concrete producers.

Storage and Dispatch

Cement is stored at the cement manufacturing facility or a cement terminal until it is shipped to a customer. Storage of bulk cement is in watertight bins or silos. About 40% of manufactured cement is shipped by rail and barge to directly to terminals. Direct customer shipments are predominately made by truck. All transportation vehicles should be equipped with watertight, properly sealed compartments. Cement is very moisture-sensitive and must be stored in a dry environment. When kept dry it will retain its quality indefinitely. If stored in contact with damp air or moisture, cement will set more slowly and have lower concrete strength than dry cement. Cement stored for long periods of time should undergo standardized tests for strength and loss on ignition before use.

Concrete

Concrete is produced by mixing cement with fine aggregate (sand), coarse aggregate (gravel or crushed stone), and water. Small amounts of chemicals, called admixtures, are frequently added to the concrete mix to control setting time and plasticity. A properly designed concrete mixture will possess the desired workability for the fresh concrete and the required durability and strength for the hardened concrete. Typically, a concrete mix is by volume about 10% to 15% cement, 60% to 75% aggregates and 15% to 20% water. Entrained air bubbles in many concrete mixtures may also take up another 5% to 8% of the volume. Table 7 shows a typical weight percent mix. The character of concrete is determined by the quality of the cement and the mix ratios. Higher-quality concrete is produced by lowering the water-cement ratio as much as possible without sacrificing the workability of fresh concrete.



When water is added to the concrete mix, it combines with the cement to form a slurry or gel that coats the surfaces of the aggregate and fills the voids of the concrete mix. The water and cement compounds undergo hydration reactions that slowly form the complex hydrated microstructure that sets the concrete and makes it solid. These reactions continue after the concrete is set and are not complete for months (and even years) after placement. The microstructure of the cement hydrates determine the mechanical behavior and durability of the concrete.

The strength developed in concrete depends on its composition and the fineness to which the cement is ground. Cements high in C_3S ($3CaO \cdot SiO_2$), especially those that are finely ground, will hydrate more rapidly and lead to higher early strength. However, rapid hydration can lead to a lower final strength. C_3S is mainly responsible for the strength developed in the first week of hardening. Cements high in C_2S ($2CaO \cdot SiO_2$) will hydrate much more slowly, leading to a denser structure with higher long-term strength. The alumina and iron compounds in cement make little contribution to final strength.

Table 7 - Typical Concrete Mix

<i>Component</i>	<i>Weight %</i>
Portland cement	12%
Sand	34%
Crushed stone	48%
Water	6%

Source: National Ready Mix Concrete Association

Concrete can deteriorate from attack by some natural or artificial chemicals. The alumina compound C_3A ($3CaO \cdot Al_2O_3$) is the most vulnerable to chemical attack in damp soils containing sulphate salts or in seawater, while the iron compound C_4AF ($4CaO \cdot Al_2O_3 \cdot Fe_2O_3$) and the two calcium silicates (C_3S and C_2S) are more resistant.

Cement liberates heat when it hydrates. Consequently, concrete placed in large masses, as in dams, can cause the temperature inside the mass to rise as much as 72°F (40°C) above the outside temperature. Subsequent thermal stresses when cooling cause cracking in the concrete

structure. The highest heat of hydration is shown by C_3A , followed in descending order by C_3S , C_4AF , and C_2S .

Ready mixed concrete consisting of cement, aggregates, water, and admixtures mixed at local plants for delivery to a work site by truck accounts for over 75% of all concrete production. Concrete masonry (e.g., 8 x 16 inch blocks) and other precast concrete products (e.g., pipes) account for 13%, contractor (on-site concrete mixing) accounts for 6%, and the remaining 6% of concrete production is used in well lining, mining operations, and other activities.

Ready mixed facilities store, convey, measure, and discharge cement, aggregates and admixtures into trucks for transport to a job site. These facilities typically receive raw materials by rail, truck, or barge. Cement is transferred and stored in elevated dry-storage silos. Sand and coarse aggregate are stored and transferred to elevated bins as needed. The raw materials are typically fed by gravity into weigh hoppers, where they are proportioned in the exact amounts specified for the concrete mix. Approximately 75% of ready mixed concrete is “transit mixed.” Transit mix trucks are loaded with sand, aggregate, cement, and water by gravity from weigh hoppers. The materials are mixed and blended in a rotating truck mounted drum while being transported to a work site. About 25% of the ready mixed concrete is blended at the ready mixed facility. The premixed and blended concrete is placed in open bed dump or agitator trucks for transport to a work site. Dry batching, with concrete mixed and hauled to the construction site dry is uncommon.

The water, sand, and gravel or crushed stone used in ready mixed concrete production are abundant and usually sourced as close to the ready mixed plant as possible. The distance and quality of the sources have an impact on transportation energy use (costs), water use for washing, and dust generation. The energy consumed for ready mixed concrete production are associated mostly with three operations (Appendix A Table A.13):

- | | |
|---|--------------------------|
| • Quarrying (fine and course aggregates) | 160,700 Btu/tonne cement |
| • Mixing and blending (cement, aggregates and admixtures) | 353,700 Btu/tonne cement |
| • Transporting the concrete mix to the work site | 697,300 Btu/tonne cement |

Ready mixed concrete production from U.S. manufactured cement is estimated to have consumed about 117.7×10^{12} Btu in 2001, approximately 1,211,700 Btu/tonne of cement (Appendix A Table A.13).

Concrete block, pipe and other precast products follow the same production steps (quarrying and blending) as ready mixed concrete, but are cast at a manufacturing site and then transported to the work site. Hence, the total energy requirement for precast product is similar to ready mixed. The difference between the two products is location of where the concrete sets. Likewise contractor, well-lining concrete operations, and mining concrete all transport quarried aggregates and then blend on the work site. These operations result in overall energy use and emissions similar to ready mixed concrete. For simplicity, this report uses the ready mixed energy use and emissions data to calculate values for all industrial concrete products. Hence, in

total, the quarrying, mixing, and transportation operations account for 2.6% (14.3×10^{12} Btu/yr), 5.7% (31.4×10^{12} Btu/yr), and 11.2% (62.0×10^{12} Btu/yr), respectively, of the on-site energy use for all cement and concrete (Appendix A Table A.10).

CO₂ emissions associated with concrete production can be calculated based on the fuels used. The three major concrete operations, quarrying, blending, and transportation, account for 1.2%, 5.4%, and 4.3% respectively, a total of 10.9% of the CO₂ emissions associated with both cement manufacturing and concrete production (Appendix A Table A.10). CO₂ emissions for concrete relative to energy usage are smaller than for cement manufacturing, which produces CO₂ from both reaction chemistry and fuel use.

Opportunities for Improving Energy Efficiency and Reducing CO₂ Emissions

Many opportunities exist for improving energy efficiency and reducing CO₂ emissions in the cement/concrete industry. These opportunities come from both changes in the manufacturing and production processes and from changes in the chemical formulation of cement. Process changes range from energy management improvements to investments in equipment upgrades or new technologies. Formulation changes have been demonstrated to save energy and reduce emissions but their widespread adoption is slowed by the burdens of developing new industrial standards.

The largest opportunities for improving energy efficiency and reducing CO₂ emissions related to energy inputs in the cement/concrete industry are mostly related to cement manufacturing. Table 8 lists the annual energy use and emissions associated with cement/concrete industry. Pyroprocessing accounts for 74% of the cement/concrete industries' energy consumption (93% of cement's manufacturing energy requirement) and operates at roughly 34% thermal efficiency. This low thermal efficiency provides many opportunities to improve performance. If it were possible to operate at the theoretical minimum energy requirements to produce clinker, nearly 400 x 10¹² Btu per year (0.4 quad) in energy savings could be obtained. Realistic and cost-effective energy savings are smaller, but achievable.

Grinding and milling account for 5.8% (12.3%) of cement/concrete energy consumption. These operations consume electricity and have energy efficiency ranging from 6% to 25%. They offer a large opportunity for energy reduction considering that each kWh saved on-site saves nearly 3 kWh of tacit energy at the electric generation site.

The potential opportunities for improving energy efficiency and lower emissions in quarrying and concrete production are smaller in terms of Btu and CO₂ emissions than in cement manufacturing. Quarrying and

Table 8 - Annual Energy Use and CO₂ Emissions Associated with Cement and Concrete Production

	On-site Energy		CO ₂ Emissions	
	10 ⁹ Btu	%	10 ⁶ tonne	%
RAW MATERIALS: QUARRYING and CRUSHING				
Cement Materials	3,817	0.7%	0.36	0.3%
Concrete Materials	14,287	2.6%	1.28	1.2%
CEMENT MANUFACTURING				
Raw Grinding	8,346	1.5%	1.50	1.4%
Kiln: fuels	410,464	74.0%	38.47	36.8%
reactions			48.35	46.3%
Finish Milling	24,057	4.3%	4.32	4.1%
CONCRETE PRODUCTION				
Blending, Mixing	31,444	5.7%	5.65	5.4%
Transportation	61,933	11.2%	4.53	4.3%
TOTAL	554,409	100%	104.50	100%

See: Appendix A Table A.10

transportation related to concrete production consume significant quantities of diesel fuel, approximately 74×10^{12} Btu/year (550×10^6 gallons). Replacement of diesel fuel with biodiesel offers an opportunity to effectively lower lifecycle emission profiles. Biodiesel is a renewable energy fuel source, typically containing the mono alkyl esters of long-chain fatty acids derived from vegetable oils (commonly soybean oil) or animal fats. It can be blended at any level with petroleum diesel to create a biodiesel blend and can be used in compression-ignition (diesel) engines with little or no modifications. It has lower emissions compared to petroleum diesel, is less toxic than table salt, and bio-degrades as rapidly as sugar. Total U.S. production of biodiesel was 25.4×10^6 gallons in 2001.²³ Total U.S. production represent only 4.6% of the diesel fuel requirement of the cement/concrete industry. Hence biodiesel availability will limit the opportunity to substitute for petroleum based diesel fuel.

Normally, energy efficiency improvements proportionally reduce the emissions of CO₂ generated from fossil fuel combustion and electricity generation. However, reducing cement manufacturing CO₂ emissions by a percentage proportional to energy efficiency improvements is not possible. More than half of the CO₂ emissions associated with cement/concrete are a result of the chemical reactions necessary for converting raw materials and not a result of the energy required to produce these reactions. If a near-zero CO₂ emitting fuel (e.g., nuclear, biomass) were utilized for all pyroprocessing energy needs, then CO₂ emissions could be reduced by 54%, from approximately 104×10^6 tonnes/yr to 48×10^6 tonnes/yr. It is also possible to reduce reaction CO₂ emissions by changing the product formulation with the substitution of raw materials, which provide cement-like properties.

The opportunities for reducing energy usage and lowering environmental impact are described in the Pyroprocessing and Product Formulations sections below. Briefly, these improvements will come from:

- Managing energy more efficiently
 - ▶ performing energy assessment/audits, utilizing energy management training, and implementations programs
- Upgrading existing equipment
 - ▶ shifting to more energy-efficient processes (e.g. from wet to dry process, from dry process to preheater)
 - ▶ installing improved heat recovery systems from clinker coolers
 - ▶ installing new design high-efficiency crushing, grinding, and milling equipment
- Adopting new pyroprocessing technologies
- Performing the R&D necessary to develop new cement manufacturing processes
- Utilizing biomass fuels
- Utilizing waste fuels
- Replacing high-carbon fuels by low-carbon fuels (e.g. shifting from coal to natural gas) *(This lowers CO₂ emissions, however at current fuel prices it increases operating costs.)*

- Changing cement product formulations, applying a lower clinker to final cement mixture ratio (i.e., increasing the ratio of cement additives that do not require pyroprocessing)
- Utilizing alternative cements (mineral polymers)
- Sequestering CO₂ from the gas streams

Cement manufacturing is a highly capital intensive and competitive industry. This fact combined with the long economic life of existing facilities will constrain the rate of upgrading exiting technology or adopting new technology. The near-term energy and emission-reduction opportunities will mainly come from better energy management practices, changes to “greener” fuels, and, to a smaller degree, changes in product formulation.

PYROPROCESSING OPPORTUNITIES

The greatest opportunities in reducing energy consumption and lowering emissions associated with cement/concrete will be obtained with improvements in cement pyroprocessing. On average, pyroprocessing systems in the United States operate at about 34% thermal efficiency. This low efficiency implies that there are potentially significant process and system improvements to improve energy and environmental performance. These *process* improvements will come from better energy management, upgrading existing equipment (e.g., replacing wet kilns, upgrading to preheater and precalciners), adopting new pyroprocessing technologies (e.g., fluidized bed systems) and, in the longer term, performing the R&D necessary to develop completely new concepts for the cement manufacturing processes.

The typical energy balances for the major pyroprocessing systems are shown in Table 9. These balances show where energy losses occur (areas where no useful work is accomplished). Any area, other than the theoretical requirement, that is losing energy represents an

Table 9 - Thermal Energy Balances to Produce Clinker in Process Kilns						
	Wet Kiln		Dry Kiln		Preheater Kiln	
Energy Use Area	Btu/tonne	Percent	Btu/tonne	Percent	Btu/tonne	Percent
Theoretical Requirement	1,690,000	30.5	1,730,000	36.6	1,670,000	49.6
Exit Gas Losses	713,000	12.9	1,310,000	27.7	471,000	13.8
Evaporation of Moisture	2,120,000	38.3	285,000	6.0	223,000	6.5
Dust in Exit Gas	10,700	0.2	12,300	0.3	1,220	0
Clinker Discharge	53,700	1.0	58,000	1.2	62,400	1.8
Clinker Stack	180,000	3.3	560,000	11.8	582,000	18.4
Kiln Shell	642,000	11.6	575,000	12.1	166,000	4.9
Calcination of Waste Dust	38,600	0.7	17,500	0.4	5,870	0
Unaccounted Losses	84,300	1.5	182,000	3.8	164,000	4.8
TOTAL	5,536,000	100	4,734,000	100	3,424,000	100

Source: *The Rotary Cement Kiln*, Kurt E. Perry, Chemical Publishing Co., Inc., New York, page 107-111

opportunity for improving energy efficiency and lowering fuel-based emissions. The large energy efficiency difference between cement processes, from 5,536,000 Btu/tonne of clinker for wet process to 3,424,000 Btu/tonne of clinker for dry process with preheater, shows the significant gains that can be made by upgrading to the more efficient process. The individual energy use areas (e.g., clinker discharge, kiln shell, etc) in Table 9 show the area and the magnitude of the opportunities available from managing energy losses by improving specific

equipment or practices.

Pyroprocessing Energy Audits

Energy audits, including kiln system performance testing and calculation of mass and heat balances, are the most comprehensive approaches to improving an existing system's energy efficiency. These audits can identify specific opportunities for improving energy efficiency and lowering CO₂ emissions. A cement manufacturing energy audit should at a minimum address the energy use areas identified in Table 9 and recommend potential actions. Typically the following actions will improve energy efficiency.

- ▶ Lower kiln exit gas losses
 - install devices to provide better conductive heat transfer from the gases to the materials (e.g., kiln chains)
 - operate at optimal oxygen levels (control combustion air input)
 - optimize burner flame shape and temperature
 - improve or add additional preheater capacity
- ▶ Lower moisture absorption opportunities for raw meal and fuels (avoiding the need to evaporate adsorbed water)
- ▶ Lower dust in exhaust gases by minimizing gas turbulence (dust carries energy away from the kiln where it is captured in dust collectors. The dust is recycled into the raw meal and fed into the kiln where it is reheated.)
- ▶ Lower clinker discharge temperature (retaining more heat within the pyroprocessing system)
- ▶ Lower clinker cooler stack temperature
 - recycle excess cooler air
 - reclaim cooler air by using it for drying raw materials and fuels or preheating fuels or air
- ▶ Lower kiln radiation losses by using the correct mix and more energy efficient refractories to control kiln temperature zones
- ▶ Lower cold air leakage
 - close unnecessary openings
 - provide more energy efficient seals
 - operate with as high a primary air temperature as possible
- ▶ Optimize kiln operations to avoid upsets

Upgrading Existing Technology – The addition of preheater sections, precalcination sections, or

more efficient clinker coolers would allow less efficient operations to maximize heat recovery. The impact of upgrading can be seen by comparing the processes shown in Table 6. If all U.S. plants upgraded pyroprocessing to the technology of the best U.S. plant (a dry process, preheater with precalciner system³), the industry would lower its energy consumption by approximately 30% to approximately 3,230,000 Btu/tonne of cement and lower CO₂ emissions by 13% to 75.3 x 10⁶ tonnes/year.

Adopting New Technology – Large pilot-scale fluidized-bed kilns (200 tonnes/day) have been developed (1996) and have demonstrated significant energy savings. It is estimated that a full-scale fluidized-bed (3,000 tonnes/day) system will consume about 2,800,000 Btu/tonne of clinker – as efficient as the most advanced U.S. kiln utilizing a preheater and precalciner and 37% more efficient than the average U.S. plant. Fluidized-bed systems are estimated to have capital costs equivalent to 88% of the capital costs of a modern cement facility and operating costs equivalent to 75% of a modern cement facility’s operating costs.²⁴ They have smaller footprints and their superior combustion characteristics of fluidized beds enable the use of lower-grade, lower cost coal.

Fluidized-bed systems do not provide “*Shutdown Economics*.” That is, their operating and capital costs are not less than the operating costs of older, fully capitalized kiln-based plants. This slows their adoption by the industry, since they are likely to be considered only for future capacity expansion. The U.S. cement industry currently operates at an average 80% kiln utilization rate²⁵. Another barrier to adoption is the natural reluctance to invest in the large capital expenditures associated with new plant construction. The risks associated with building a new technology commercial-scale plant, based on the successful demonstration of a one-tenth scale facility, are considered high.

Cogeneration – Large industrial thermal energy demand offers opportunities for cogeneration of electricity and/or steam production, particularly if the cogeneration system is part of the initial plant design. Cogeneration has demonstrated that it can significantly improve the overall energy efficiency of some manufacturing operations. Five cement manufacturing plants cogenerate electricity on-site.²⁶ Currently, about 38% of U.S. cement capacity does not take advantage of preheater and/or precalciner systems. These plants typically have large heat losses (waste heat streams). Utilization of waste heat in preheater heat exchange systems is usually more energy efficient than the cogeneration of electricity with its inherently low conversion efficiency of thermal to electrical energy (typically about 9,935 Btu are required to produce 1 kWh (3,412 Btu)). Cogeneration of steam at a cement plant is possible, but typically cement plants require little steam and are located in isolated areas where markets for excess steam generation are not available.

Biomass Fuels – Trees, plants, and crops (biomass) incorporate (sequester) CO₂ as carbon compounds as they grow. On a life-cycle basis, where the life-cycle includes both the growth phase and the use phase (combustion), there is a near net-zero emission of CO₂ associated with the use of biomass fuels (Net life-cycle emissions are not zero, because energy is used to gather, increase density, reduce moisture, deliver, and store biomass fuels). Therefore the use of biomass

fuels for pyroprocessing can provide energy with low-net CO₂ emissions.

Cement pyroprocessing is suited to utilizing biomass as an ancillary fuel. Careful system design is required to account for biomass combustion characteristics (moisture load, flowability, burn temperature,...) and byproducts (ash composition). Biomass fuels do not improve energy efficiency per se, however they do replace conventional fuels and lower life-cycle CO₂ emissions. Burning biomass fuels can offer other indirect benefits:

- ▶ U.S. dependence on imported fuels is reduced,
- ▶ crops grown exclusively for energy production can provide economic opportunity for underutilized agricultural lands,
- ▶ energy crops require fewer herbicides and pesticides compared to row crops, and
- ▶ chemical runoff into surface water and groundwater is reduced.

An additional benefit of burning biomass over fossil fuels is the reduction of sulfur dioxide (SO₂) emissions. Most forms of biomass contain small amounts of sulfur; therefore, biomass being burned emits little sulfur dioxide (SO₂). For example, using biomass for 5% of a coal-fired heat input would reduce SO₂ emissions by approximately 5%. This benefit may not be fully realized in cement kiln operations. Limestone in the cement kiln's raw meal acts as a natural SO₂ scrubber resulting in low SO₂ emissions. Hence biomass fuels will not significantly change the SO₂ emissions associated with cement kiln operations.

Alternate/Waste Fuels – Utilization of alternate/waste fuels does not directly improve the energy efficiency or lower the CO₂ emissions of cement manufacturing. However, it does reduce the use of conventional fuels, lowers U.S. dependence on imported fuels, and reduces waste material sent to landfills. Depending on the alternate/waste fuel used it can be argued that there are real indirect energy savings and emission reductions. Placing a quantitative value on these indirect energy savings and emission reductions however is problematic.

Cement pyroprocessing is currently used for and highly suited to the disposal of alternate or waste fuels, such as used solvents, oils, tires, carpets, and other hazardous wastes (see fuel mix, Table 3). In the case of many hazardous wastes, cement pyroprocessing is more advantageous than commercial incinerators. Time, temperature, and turbulence are the three most important factors to ensure the destruction of organic and/or hazardous organic wastes. Cement pyroprocessing systems have a high degree of mixing, have long gas residence times, and burn hotter (30% higher than the temperatures in a commercial hazardous waste incinerator) than a typical thermal waste treatment facility. Cement kilns are very large and have a high heat capacity. Temperatures cannot change quickly due to process "upsets," ensuring that waste destruction is complete. Limestone also acts as a natural "dry scrubber" inside the kiln to capture chlorine and sulfur compounds, as well as some metals. Organic materials are completely combusted. Cement kilns easily achieve a Destruction and Removal Efficiency of at least 99.99 percent, as required by U.S. Environmental Protection Agency regulations for most organic wastes. However, care must be taken for high volatile elements (i.e., mercury, thallium, etc.).

Kilns operate with a temperature profile along their length that controls the sequence of kiln reactions and phase changes. Waste materials combust and burn at different temperatures under different conditions. Solid waste fuels need to be introduced into the kiln in such a manner as to not significantly change the temperature profile and chemical reactions. It is sometimes necessary to add solid waste through a hatch or valve structure in the kiln shell. This is technically challenging and creates an additional source of thermal and emission losses.

Receiving and handling of alternate or waste fuels can raise technical, liability, and political concerns. Cement manufacturing companies do not desire to be labeled as handlers of hazardous wastes and surrounding communities have valid concerns about hazardous waste transport and final emissions. These concerns can be difficult to address and in some cases are perceived as a financial liability to the cement manufacturer.

GRINDING AND MILLING OPPORTUNITIES

Grinding and milling operations are notoriously energy inefficient. Typical systems routinely run at 6% to 25% on-site energy efficiency.¹⁷ Although these systems do not account for a large portion of the on-site energy consumption profile of a cement plant, they do offer significant opportunities for energy improvement. Raw material grinding and finish mill systems should be evaluated for both efficiency of energy usage and cement quality. Modern finish mill systems may comprise several units of process equipment – high-pressure, twin-roll presses, tube mills, ball mills, and conventional or high-efficiency separators. Air flow, and material and heat balances should be measured and evaluated. Optimization of these systems may include:

- ▶ Adjustment of ball charges
- ▶ Studies of circulating loads
- ▶ Analyses of Tromp curves
- ▶ Modifying particle size distribution
- ▶ Controlling gypsum dehydration

PRODUCT FORMULATION CHANGES TO IMPROVE ENERGY EFFICIENCY

Energy efficiency improvements and emission reductions can also result from changes in the *Product Formulation* of cement. Research has shown that energy-saving modifications are possible without a loss in concrete performance. These modifications include the addition of limestone and other cement-like materials (e.g., fly ash, furnace slag, or other pozzolanic materials) that do not require the large energy inputs and emissions associated with pyroprocessing.

Changes to cement product formulations require significant time to be incorporated into ASTM standards and be accepted in the marketplace. An ASTM committee (C01.10) is considering a proposal to allow 5% limestone in portland cement. This formulation is supported with over thirty years of research and 20 years of field experience that confirms that this formulation change meets all chemical and physical property requirements. Current European (EN197) and Canadian (CSA A5) specifications allow this formulation. This change in product formulation results in roughly a 5% decrease in energy use and a 2.6% reduction in CO₂ emissions. Concrete producers specify cement based on ASTM standards in order to guarantee the performance characteristics of concrete. Changes to these formulations are perceived as “risky” because change represents a move away from standards that have a long and well-documented performance history.

Pozzolan

Materials that can be added to cement to extend its volume without a significant loss of properties are known as “pozzolans.” They are named after the ash deposits adjacent to the Pozzol volcano that the Romans used as cement. The Pantheon in Rome is a testament to the high strength and durability of pozzolan cement. Its hemispherical dome, 141 feet (43 meters) in diameter, is made completely from pozzollan cement and does not contain any reinforcing bars. It has been in use since 135 A.D. (for comparison the U.S. Capital dome is 96 feet in diameter)

The addition of pozzolan to cement will modify its characteristics. Depending on the type of pozzolan chosen, the density and compressive strength of the formed concrete may be increased and porosity reduced. Pozzolanic materials can combine with uncarbonated lime (calcium hydroxide) to form stable compounds, thus reducing the risk of early leaching or frost damage and increasing the potential durability of the mortar.

Pozzolan materials, in general, do not require pyroprocessing and, hence, can save very significant quantities of energy and lower emissions when supplementing regular cement. Concrete research is now calling for increased usage and high-volume usage of pozzolans, especially fly ash. Some have suggested that *all* concrete should contain fly ash²⁷. The economic and environmental advantages of adding pozzolan would seem to indicate that their regular and high-volume use will become standard practice in the concrete industry. The U.S. Environmental Protection Agency requires fly ash content in concrete to be used in buildings that receive

federal funding.

Coal-fired power fly ash is sometimes used as a source of silica in cement manufacturing, but more commonly is used in concrete production as a substitute for a portion of the cement. This is beneficial in two ways: it reduces solid waste and overall energy use since it does not require pyroprocessing. Fly ash can readily be substituted for 15% to 35% of the cement in concrete mixes and in some applications fly ash content can be up to 70%. These additions change the performance characteristics of the concrete. Of the 68 million short tons of coal fly ash produced in 2001, 12.4 million short tons were used in cement and concrete products²⁸. Fly ash can contain elements (e.g., carbon), compounds (e.g., ammonia) and other constituents that are detrimental to concrete performance.

Fly ash and slags react with any free lime left after the hydration to form calcium silicate hydrate, which is similar to the tricalcium and dicalcium silicates formed in cement curing. This process increases strength, improves sulfate resistance, decreases permeability, reduces the water ratio required, and improves the pumpability and workability of the concrete. Western coal-fired power plants produce better fly ash for concrete than eastern plants, because of lower sulfur and lower carbon content in the ash. Fly ash from incinerators cannot be used. Portland cement with fly ash added is sometimes identified with the letter P after the type number (e.g., Type IP).

Other industrial waste products, including blast furnace slag, cinders, silica fume and steel mill scale are sometimes substituted for some of the aggregate in concrete mix. Recycled concrete can be crushed into aggregate and reused in the concrete mix. However, the irregular and higher surface area of crushed concrete aggregate is more costly than sand or crushed stone because it takes more cement slurry to coat the surface.

Endnotes:

1. *Emission of Greenhouse Gases in the United States 2001*, Energy Information Agency, DOE, December 2002, page 31
2. *Cement Manufacturing*, Energy Solutions Center, Inc. Washington, DC, Copyright DTE Energy, TechPro©2001, Version 1.1, October 2002
3. *Concrete: Sustainability and Life Cycle - Life Cycle Research Reports 1994 through 2000*
This CD contains 31 reports with a focus on concrete. Cement is a key component in a LCA and data are presented in many of these reports.
4. *2000 U.S. AND CANADIAN LABOR-ENERGY INPUT SURVEY*, Portland Cement Association, March 2002, page 3
5. *Emission of Greenhouse Gases in the United States 2001*, page 31
6. *Integrated Pollution Prevention and Control (IPPC) Reference Document on Best Available Techniques in the Cement and Lime Manufacturing Industries*, March 2001, European Commission, Directorate-General Joint Research Centre, Institute for Prospective Technological Studies, Technology for Sustainable Development, European IPPC Bureau, page 26
7. *Integrated Pollution Prevention and Control (IPPC) Reference Document on Best Available Techniques in the Cement and Lime Manufacturing Industries*, page 27
8. *Integrated Pollution Prevention and Control (IPPC) Reference Document on Best Available Techniques in the Cement and Lime Manufacturing Industries*, page 27
9. *Mineral Commodity Summaries*, U.S. Geological Survey, Jan 2003, page 44
10. *Cement U.S. Geological Survey Minerals Yearbook -2001*, Hendrik G. van Oss, page 16.1
11. *U.S. Cement Industry Factsheet*, Portland Cement Association, II, 2002 Edition Update, Table 17
12. *U.S. Cement Industry Factsheet*, Table 14
13. *U.S. Cement Industry Factsheet*, page 14
14. *Ready Mixed Concrete Industry: An Integral Part of the American Economy*, National Ready Mixed Concrete Association, Washington, DC. January, 2002
15. *Cement U.S. Geological Survey Minerals Yearbook -2001*, Table 16

16. *Encyclopedia of Chemical Technology*, Kirk-Othmer, 3rd edition 1979, John Wiley & Sons, NY, NY, Volume 5, page 165
17. *Encyclopedia of Chemical Technology*, Volume 14, page 343
18. *Energy and Environmental Profile of the U.S. Mining Industry*, U.S. Department of Energy, Office of Industrial Technologies, Mining Industry of the Future, page 9-8.
19. *Energy and Environmental Profile of the U.S. Mining Industry*, page 9-8
20. *Chemical Engineering Handbook*, Fourth edition, John H. Perry, McGraw-Hill Book Company, page 8-8
21. *The Rotary Cement Kiln*, Kurt E. Perry, 1986, Chemical Publishing Co., Inc., New York, page 107
22. *Chemical Engineering Handbook*, page 8-8
23. *Alternatives to Traditional Fuels* 2000, September 2002 U.S. Department of Energy, table 10
24. Kawasaki Heavy Industries, Ltd. website (<http://www.khi.co.jp/products/sanki/san/faks.htm>) FAKS (Fluidized Bed Advanced Cement Kiln System)
25. *U.S. Cement Industry Factsheet*, Portland Cement Association, II, 2002 Edition Update, Table 14
26. *Cement U.S. Geological Survey Minerals Yearbook -2001*, Hendrik G. van Oss, Table 8
27. *Mineral Admixtures*, John Scanlon, ACI Compilation 22, 1992
28. *2001 Coal Combustion Product Survey*, American Coal Ash Association, Aurora, CO

Table A.1 - Cement Manufacturing by Pyroprocess System

Note: This table provides kiln information based on survey data collected by the Portland Cement Association. It represents approximately 95% of the U.S. cement manufacturing companies, 92% of U.S. production and 93% of U.S. kilns. In total the United States has 204 operating kilns and produced 78,451,000 metric tons in 2001 (U.S. Geological Survey Minerals Yearbook - 2001, Cement, Hendrick G. van Oss, Table 5).

	Number of Kilns	Percent Kilns	Metric Tonnes clinker produced in 2001	Percent Tonnes
Wet Process	54	28.4%	14,029,433	19.5%
Dry Process	136	71.6%	57,831,070	80.5%
No Preheater or Precaliner	59	31.1%	12,953,759	18.0%
Preheater/Precaliner	77	40.5%	44,877,311	62.5%
Preheater Only	35	18.4%	13,832,465	19.2%
Precaliner	42	22.1%	31,044,846	43.2%
Total	190	100%	71,860,503	100%

Source: 2000 U.S. and Canadian Labor-Energy Input Survey, Portland Cement Association

Table A.2 - Total U.S. Clinker and Cement Supply based on 2001 data from the U.S. Geological Minerals Yearbooks

78,451,000	U. S Clinker Manufacturing	a
1,884,000	U.S. Clinker Imports	b
80,335,000	Total U.S. Clinker Manufacturing and Imports	c
84,450,000	Total U.S. Building/Portland Cements	d
4,450,000	Total U.S. Masonry Cements	e
88,900,000	Total U.S. Cement (USGS)	f
91,037,000	Total U.S. Cement (PCA)	g

Sources:

- a - U.S. Geological Survey Minerals Yearbook - 2001, Cement, Hendrick G. van Oss, Table 5
- b - U.S. Geological Survey Minerals Yearbook - 2001, Cement, Hendrick G. van Oss, Table 12
- c - Sum of U.S. Clinker Manufacturing and Imports
- d - U.S. Geological Survey Minerals Yearbook - 2001, Cement, Hendrick G. van Oss, Table 3
- e - U.S. Geological Survey Minerals Yearbook - 2001, Cement, Hendrick G. van Oss, Table 4
- f - sum of Portland and Masonry Cements
- g - For comparison: 2001 Portland and Masonry Cements total from *United States Cement Industry Fact Sheet 2003*, Portland Cement Association

**Table A.3 - Raw Materials (non-fuel) for Clinker and Cement Production
in the United States and Puerto Rico**

	2001 Clinker			2001 Cement	
	tonnes (a)	%	loss on ignition percent (b)	tonnes (a)	non - clinker percent
Calcareous					
Limestone	95,600,000	70.6%	43.7%	1,600,000	22.2%
Cement Rock	21,900,000	16.2%	37.2%	100,000	1.4%
Kiln Dust	600,000	0.4%		100,000	1.4%
Lime	300,000	0.2%		40,000	0.6%
Other	20,000	0.0%		20,000	0.3%
Aluminous					
Clay	4,500,000	3.3%	8.0%	10,000	0.1%
Shale	3,200,000	2.4%	8.2%	10,000	0.1%
Other (includes: bauxite, alumina, aluminum dross, ...)	500,000	0.4%			
Ferrous					
Iron Ore, Pyrites, Other	1,500,000	1.1%			
Siliceous					
Sand and Calcium Silicate	3,500,000	2.6%	6.6%		
Sandstone, Quartzite, Other	500,000	0.4%			
Fly Ash	1,600,000	1.2%		70,000	1.0%
Other Ash	800,000	0.6%			
Blast Furnace slag	200,000	0.1%		300,000	4.2%
Steel slag	500,000	0.4%			
Other slags	50,000	0.0%		5,000	0.1%
Pozzolans	100,000	0.1%		59,000	0.8%
Miscellaneous	40,000	0.0%		50,000	0.7%
TOTAL Raw Materials for Clinker Manufacturing	135,410,000	100%			
Total Clinker Manufactured - based on kiln processing ignition losses for limestone, cement rock and other raw materials (c)	84,831,000	63%			
Total CO₂ Emissions (d)	49,924,000	37%			
Cement Non-Clinker Raw Materials, continued					
Gypsum				4,800,000	66.5%
Other				50,000	0.7%
Total non-Clinker Materials				7,214,000	100%
Cement Raw Materials				tonnes	percent
Total non-Clinker Materials				7,214,000	8%
Imported Clinker				2,950,000	3%
Clinker Manufactured (c)				84,831,000	89%
TOTAL Cement Production				94,995,000	100%

Source:

a - U.S. Geological Survey Minerals Yearbook - 2001, Cement, Hendrick G. van Oss, Table 6

b - Encyclopedia of Chemical Technology, 3rd Edition, Kirk-Othmer, John Wiley & Sons, NY, NY 1979, Vol 5 page 171

c - Calculated weight loss based on ignition losses. Ignition loss is a measure of the CO₂, H₂O and other products release at high temperature. Ignition loss data are available for 93% of the raw material. Ignition loss values for the remaining raw materials are assumed to be small.

d - CO₂ emissions assumes that ignition losses for limestone (43.7%) and cement rock (37.2%) are all CO₂. (Note: CO₂ accounts for 44% of pure CaCO₃ ignition loss.)

Table A.4 Important Ratios and Numbers for Raw Materials**Quarried Clinker Raw Materials**

131,660,000	Quarried Clinker Raw Materials (total minus kiln dust, ash and slag)
1.434	Mass Ratio of Quarried Clinker Raw Materials to Cement Manufactured
1.552	Mass Ratio of Quarried Clinker Raw Materials to Clinker Manufactured
1.127	Mass Ratio of Limestone Quarried to Clinker Manufactured
1.785	Mass Ratio of CaCO ₃ to CaO
1.776	Mass Ignition Ratio for limestone (before/after)

Quarried Cement Raw Materials

6,739,000	Quarried Cement Raw Materials (total minus kiln dust, ash and slag)
0.071	Mass Ratio of Quarried Cement Raw Material to Cement

Calcine Reaction Data

0.589	Ratio for chemical reaction tonne of CO ₂ per tonne of manufactured
0.544	Ratio for chemical reaction tonne of CO ₂ per tonne of manufactured

Source: Values are based on the data presented in Table A.3

Table A.5 - Energy Use Associated with Limestone Quarrying

	Btu/tonne Limestone	Tacit Btu/tonne Limestone	Primary Fuel	kilogram CO₂ per tonne Limestone (a)
QUARRYING				
Percussion Drill	6,140	6,377	Diesel	0.4491
Hydraulic Shovel	5,670	5,888	Diesel	0.4148
Rear-Dump Truck	4,030	4,185	Diesel	0.2948
Bulldozer	3,420	3,552	Diesel	0.2502
Pick-Up Trucks	2,250	2,468	Gasoline	0.1596
Water Tanker	1,170	1,215	Diesel	0.0856
Service Truck	1,120	1,163	Diesel	0.0819
Lighting Plant	66	192	Electric	0.0119
Front-End Loader	187	194	Diesel	0.0137
Bulk Truck	147	153	Diesel	0.0108
Pumps	2,250	6,548	Electric	0.4044
Grader	7	7	Diesel	0.0005
subtotal	26,457	31,943		2.1772
BENEFICIATION				
Conveyor	182	530	Electric	0.0327
Screens	366	1,065	Electric	0.0658
Primary Crushers	1,830	5,326	Electric	0.3289
Secondary Crushers	1,097	3,193	Electric	0.1972
subtotal	3,475	10,113		0.6246
TOTAL	29,932	42,056		2.8017

Source: *Energy and Environmental Profile of the U.S. Mining Industry*, U.S. Department of Energy, Industrial Technologies Program, page 9-9

a - Carbon dioxide emissions are calculated based on the Btu/tonne of limestone times the carbon emission equivalent in Table A.15 for the specific fuel times the ratio of CO₂ to C (44/12).

**Table A.6 - Energy Associated With Quarrying Raw Materials
Necessary to Manufacture Cement**

These values assume that all quarried raw materials used in cement manufacturing require the same energy per mass as does limestone quarrying	Quarrying Energy Btu/tonne cement a	Quarrying Energy Tacit Btu/tonne cement b		Quarrying kilogram CO ₂ per tonne cement c
	42,931	60,321		4.02

a - Btu per tonne of limestone from Table A.5 multiplied by 1.43 which is the mass ratio of quarried clinker raw materials to cement manufactured from U.S. manufactured clinker Table A.3.

b - Same as (a) but using tacit energy values from Table A.5

c - Same as (a) but using carbon dioxide emission values from Table A.5

**Table A.7 - Energy Associated With Quarrying Raw Materials
Necessary for the Production of Concrete**

These values assume energy ratios described below.	Mass Quantity Relative to Cement a	Quarrying Energy Btu/tonne cement b	Quarrying Energy Tacit Btu/tonne cement c	Quarrying kilogram CO ₂ per tonne cement d
Sand	2.83	59,118	76,956	5.18
Gravel or Crushed Stone	4.00	101,594	138,434	9.26
TOTAL		160,712	215,389	14.43

a - Common weight ratio of concrete raw materials to cement for ready mixed cement is used for all cement products (34% sand to 12% cement) (48% crushed stone to 12% cement).

b - For the raw material sand, this value is assume to be equal to limestone quarrying energy less the percussion drilling, primary and secondary crushing operations. For gravel or crushed stone, this value is assumed to be equal to limestone quarrying energy less half of the percussion drilling, primary and secondary crushing operations.

c - Tacit adjust uses the same basis described in (b) above.

d - Carbon dioxide emission use Table A.5 values adjusted for the basis described in (b) above.

Table A.8 - Energy Consumed by Fuel Type in Cement Manufacturing (excluding Quarrying)

2001 U.S. Annual tonnes, Table A.2		All Plants 10 ⁹ Btu (a)	Fuel Percentage %	Tacit All Plants 10 ⁹ Btu (b)	Fuel Percentage %	CO ₂ emissions 10 ⁶ tonnes (d)
Clinker Production	78,451,000					
Cement Production	88,900,000					
FUELS						
Coal		265,284	60%	266,703	50%	24.931
Petroleum Coke		67,628	15%	67,628	13%	6.906
Natural Gas		23,258	5%	23,326	4%	1.234
Middle Distillates		3,500	1%	3,626	1%	0.266
Residual Oil		344	0%	355	0%	0.027
Gasoline		407	0%	447	0%	0.029
LPG		25	0%	25	0%	0.002
WASTE FUELS						
Oils		1,334	0%	1,334	0%	0.086
Solvents		22,397	5%	22,397	4%	1.081
Tires		10,258	2%	10,258	2%	1.218
Solids		1,119	0%	1,119	0%	0.082
Misc.		673	0%	673	0%	0.049
Subtotal		396,226	89%	397,890		35.911
ELECTRICITY						
Raw Material Grinding (c)		8,346	2%	24,291	5%	
Pyroprocessing		14,238	3%	41,437	8%	
Finish Milling (c)		24,057	5%	70,014	13%	
Subtotal		46,642	11%	135,742		8.383
TOTAL		442,868	100%	533,632	100%	44.29

a - These values are adjusted to reflect the entire 2001 U.S. production of cement shown in Table A.2 (88,900,000 tonne). The data are based on Btu/tonne of cement values reported in the *2000 U.S. and Canadian Labor-Energy Input Survey*, by Portland Cement Association, page 12. These are based on surveys of approximately 90% of U.S. capacity.

b - Tacit values are calculated using the "All Plants" data multiplied by the appropriate tacit correction factor listed in Table

c - Electricity is proportioned by applying percentages used in *The Reduction of Resource Input and Emissions Achieved by the Addition of Limestone to Portland Cement*, M. A. Nesbit, Portland Cement Association, 1996, page 6.

d - Carbon dioxide emissions are calculated based on the Btu value times the carbon emission equivalent in Table A.15 for the specific fuel times the ratio of CO₂ to C (44/12).

**Table A.9 - Fuel and CO₂ Differences in Cement Manufacturing
between 1971 and 2000**

	1971		2000	
	Onsite Production Btu/tonne Cement	CO ₂ Production tonne/tonne Cement	Onsite Energy Use Btu/tonne Cement	CO ₂ Production tonne/tonne Cement
FUELS				
Coal	2,639,000	0.2480	2,984,100	0.2804
Petroleum Coke	39,600	0.0040	760,700	0.0777
Natural Gas	3,347,100	0.1776	261,600	0.0139
Middle Distillates	88,300	0.0065	39,400	0.0029
Residual Oil	808,900	0.0631	3,900	0.0003
Gasoline	7,400	0.0005	4,600	0.0003
LPG	1,400	0.0001	280	0.0000
WASTE FUELS				
Oils	0		15,000	0.0010
Solvents	0		251,900	0.0122
Tires	0		115,400	0.0137
Solids	0		12,600	0.0009
Misc.	0		7,600	0.0006
FUELS Subtotal	6,931,700	0.4999	4,457,080	0.4038
ELECTRICITY	488,600	0.0878	524,700	0.0943
TOTAL	7,420,300	0.5877	4,981,780	0.4982
Decrease in energy and emissions levels from 1971 to 2000				
				33% 15%
Total CO ₂ Emissions are a function of the fuels used. If year 2000 cement manufacturing plants used the 1971 fuel mix ratio, CO ₂ emission would be lower by 21% in year 2000.				
Btu/tonne of cement			4,981,780	0.3945
Percent change			0%	21%

Source: Cement Industry Fact Sheet 2002 edition, Portland Cement Association

Table A.10 - Annual Energy Use Associated with U.S. Cement Manufacturing and Concrete Production from U.S. Cement

Kiln operations, pyroprocessing, accounts for the vast majority of energy consumption and CO₂ emissions in the cement and concrete industries. Kilns consume 74.2% of the energy and produce 81.3% of the CO₂ emissions associated with the cement and concrete industries. Kilns consume 82% of the energy and produce 94% of the CO₂ emissions associated with the cement manufacturing.

	Onsite Annual Energy Use 10 ⁹ Btu	Tacit Annual Energy Use 10 ⁹ Btu	Annual CO ₂ Production 10 ⁶ tonnes	Onsite Annual Energy Use %	Tacit Annual Energy Use %	Annual CO ₂ Production %
Quarrying						
cement raw materials (a)	3,817	5,363	0.36	0.7%	0.7%	0.3%
concrete raw materials (b)	14,287	19,148	1.28	2.6%	2.5%	1.2%
Cement Manufacturing (c)						
raw material grinding	8,346	24,291	1.50	1.5%	3.2%	1.4%
kiln fuels	410,464	439,327	38.47	74.0%	57.4%	36.8%
kiln reactions (d)			48.35			46.3%
finish milling	24,057	70,014	4.32	4.3%	9.1%	4.1%
Concrete Production (e)						
raw material mixing	31,444	122,017	5.65	5.7%	15.9%	5.4%
transport	61,993	85,842	4.53	11.2%	11.2%	4.3%
Total	554,409	766,001	104.5	100%	100%	100%

a - Values from Table A.6 adjusted for U.S.G.S. cement production estimates for 2001

b - Values from Table A.7 adjusted for U.S.G.S. cement production estimates for 2001

c - Values from Table A.8

d - Values from Table A.3 and A.4

e - Values from Table A.13 adjusted for the assumption that all concrete energy use and emissions will be equivalent to ready mix values

Table A.11 - Energy Use per Tonne Associated with U.S. Cement Manufacturing and Concrete Production from U.S. Cement

	Onsite Energy Use Btu/tonne Cement	Tacit Energy Use Btu/tonne Cement	CO ₂ Production tonne/tonne Cement	Onsite Energy Use %	Tacit Energy Use %	CO ₂ Production %
Quarrying						
cement raw materials (a)	42,931	60,321	0.0040	0.7%	0.8%	0.3%
concrete raw materials (b)	160,712	215,389	0.0144	2.6%	2.7%	1.2%
Cement Manufacturing (c)						
raw material grinding	93,885	273,235	0.0169	1.5%	3.4%	1.4%
kiln fuels	4,617,146	4,941,815	0.4327	74.0%	61.5%	36.8%
kiln reactions (d)			0.5438			46.3%
finish milling	270,610	787,561	0.0486	4.3%	9.8%	4.1%
Concrete Production (e)						
raw material mixing	353,704	1,029,390	0.0636	5.7%	12.8%	5.4%
transport	697,337	724,198	0.0510	11.2%	9.0%	4.3%
Total	6,236,325	8,031,910	1.1751	100%	100%	100%

a - Values from Table A.6

b - Values from Table A.7

c - Values from Table A.8 adjusted for U.S.G.S. cement production estimates for 2001

d - Values from Table A.3 and A.4

e - Values from Table A.13 adjusted for U.S.G.S cement production estimates for 2001 adjusted for the assumption that all concrete energy use and emissions will be equivalent to ready mix values

Table A.12 - Costs Associated with Ready Mixed Concrete Production

2002 Cubic Yards 390,646,000	Cost Range	
	\$/yd	\$/yd
Utilities	\$0.75	\$1.00
Fuel	\$1.18	\$2.09
Environmental	\$0.05	\$0.10
Sales Price	\$65.00	\$80.00

Source: Based on information provided in a conversation with Mr Herbert of the National Ready Mix Concrete Association

Table A.13 - Projection of Energy Consumption for Ready Mixed Concrete Using Average of Cost Range Values for Ready Mixed Concrete Table A.12 and Quarrying Data from Table A.7

	Annual Cost	10 ⁹ Btu/yr	Btu/tonne of Cement	Tacit Btu/tonne of Cement	kg CO ₂ per tonne of Cement
	a	b	c	d	e
Quarrying ¹		13,248	160,712	215,389	14.4
Mixing & Blending ²	\$ 341,815,250	29,157	353,704	1,029,390	63.6
Transportation ³	\$ 638,706,210	57,484	697,337	724,198	51.0
TOTAL		99,888	1,211,753	1,968,978	129

Note: the total Btu consumed per year are higher in this table for concrete operations than the values shown in Table A.10. This table is based on the combined total of U.S. manufactured cement and imported cement.

1- The data for ready mixed quarrying energy requirements is based on the quarrying energy requirements developed in Table A.7 multiplied by the proportion of the cement market that goes into ready mixed.

The cement ready mixed portion is 75%

2- Mixing and Blending operations are predominately electric based and are assumed to be fully reflected in the utility cost in Table A.12

3- Fuel costs in Table A.12 are predominately related to Transportation of the mixed/blended aggregate and cement plus water to the work site. Diesel is the predominate fuel.

a - average price multiplied by annual production from Table A.12

b - annual cost (a) divided by cost per energy unit - electric \$0.04 \$/kWh or \$/(3,412 Btu)
- fuel \$1.50 \$/gal

c - Btu/yr (b) divided by the cement required to produce concrete using the values:

2,300 kg/m³ for concrete

and 12% weight cement to concrete

d - Btu/tonne of cement (c) times tacit correction factor from Table A.14 (Fuel assume to be diesel)

e - Annual CO₂ production based on the "c" column times the carbon emission equivalent in Table A.15 value for the specific fuel times the ratio of CO₂ to C (44/12).

Table A.14 - Calorific and Process Energy Values Associated with Fuels

Calorific energy values are the energy content inherent to the material. Except for pure materials, e.g., propane, these values vary depending on the raw materials used and the final products formulations.

Process energy is a measure of the energy required to manufacture the material. Process Energy values are also variable and depend on equipment efficiency estimates and system boundaries. These values for crude oil-derived products are variable and depend on the specific crude processed, refinery configuration, local product specifications, and refinery efficiency. Process energy values from the CEC include the energy for processing, as well as factors for raw material, e.g. delivery of crude to refiners and transporting fuels to their point of use.

Tacit or gross energy is the sum of the calorific and process energy values. The Tacit Correction factor is the ratio of the Tacit Energy value divided by the inherent or calorific energy value.

Cement concrete input units		Calorific Energy Values "Primary-Energy"				Process Energy Values "Secondary-Energy"			Tacit Energy	Tacit Correction Factor
		FUELS							Btu per	Input
		Data	Btu per			Btu per Common	Data	Btu per		
		Btu per Common Unit	Source	Input Unit	Unit Required to Produce	Source	Input Unit	input unit	Unit	
		Fuels and Fuels used as materials								
Coal, Industrial	short ton	22,433,000 Btu/ton	AEO2003	22,433,000	60 Btu/lb	E&E, Mining	120,000	22,553,000	1.005	
Coal, electric utility	short ton	20,511,000 Btu/ton	AEO2003	20,511,000	60 Btu/lb	E&E, Mining	120,000	20,631,000	1.006	
Bituminous/Sub	short ton	11,110 Btu/lb	CIA2000	22,220,000	60 Btu/lb	E&E, Mining	120,000	22,340,000	1.005	
Petroleum Coke	short ton	30,120,000 Btu/ton	MECS	30,120,000				30,120,000	1.000	
Green Coke	short ton	14,200 Btu/lb	MidCon	28,400,000	Btu/lb	Drexel		28,400,000	1.000	
Calcined Coke	short ton	15,250 Btu/lb	MidCon	30,500,000	179 Btu/lb	E&E pg 52	358,000	30,858,000	1.012	
Pitch										
Natural Gas	million ft3	1,027 Btu/ft ³	AEO2003	1,027,000,000	30 Btu/ft3		3,000,000	1,030,000,000	1.003	
Fuel Oil, light	gallon	150,000 Btu/gal	cogeneration.net	150,000	5,000 Btu/gal	Drexel	5,000	155,000	1.033	
Fuel Oil, medium	gallon	139,000 Btu/gal	cogeneration.net	139,000	5,000 Btu/gal	Drexel	5,000	144,000	1.036	
Residual Fuel Oil	gallon	6,287,000 Btu/bbl	AEO2003	149,690	5,000 Btu/gal	Drexel	5,000	154,690	1.033	
Distillate fuel	gallon	5,825,000 Btu/bbl	AEO2003	138,690	5,000 Btu/gal	Drexel	5,000	143,690	1.036	
Lube Oil	gallon	6,065,000 Btu/bbl	EIA	144,405	5,000 Btu/gal	Drexel	5,000	149,405	1.035	
Gasoline	gallon	5,202,000 Btu/bbl	AEO2003	123,857	12,000 Btu/gal	CEC	12,000	135,860	1.097	
Kerosene	gallon	5,670,000 Btu/bbl	AEO2003	135,000	5,200 Btu/gal	CEC	5,200	140,200	1.039	
Diesel	gallon	5,670,000 Btu/bbl	EIA	135,000	5,200 Btu/gal	CEC	5,200	140,200	1.039	
LPG	gallon	3,603,000 Btu/bbl	AEO2003	85,786				85,790	1.000	
Propane	gallon	3,824,000 Btu/bbl	EGGUS	91,048				91,050	1.000	
Solvent	gallon	5,248,000 Btu/bbl	EIA, naphtha	124,952	12,000 Btu/gal	Drexel	12,000	136,952	1.096	
Rolling Oil	gallon	6,065,000 Btu/bbl	EIA	144,405	5,000 Btu/gal	Drexel	5,000	149,405	1.035	
WASTE -										
Oils	gallon	95 - 150,000 Btu/gal	a			b		122,500	1.000	
Solvents	gallon	85 - 100,000 Btu/gal	a			b		92,500	1.000	
Tires	ton	22 - 35,000,000 Btu/ton	a			b		28,500,000	1.000	
Solids									1.000	
Misc.									1.000	
		ELECTRICITY								
Electric		1 kWh	ISO	3,412	Hydroelectric Utility	ISO	-	3,412	1.000	
Average U.S. Electric		1 kWh	ISO	3,412	Average U.S. Grid	c	6,523	9,930	2.910	
Coal-Fired Electric		1 kWh	ISO	3,412	Coal-Fired Utility	c	7,097	10,510	3.080	

* tacit Btu accounts for generation and transmission energy losses for average U.S. generation

SOURCES

- AEO2003- Annual Energy Outlook 2003, Energy Information Administration, U.S. DOE, Jan 2003 page 249
- CEC - California Energy Commission
- CIA2000- Coal Industry Annual 2000, Energy Information Administration, Jan 2002 page 284 -This report uses an average value for bituminous and sub-bituminous coals.
- Drexel - data approximations derived from Drexel University study
- E&E - documents from DOE - OIT these are from the "Energy and Environmental Profiles" of the Aluminum and Mining Industries
- EGGUS - Emissions of Greenhouse Gases in the United States 1987-1992, Energy Information Administration, U.S. DOE, Oct 1994 Appendix A
- MidCon- Data from Mid-Continent Coal & Coke Co.
- MECS - Energy Information Administration, U.S. DOE, Manufacturing Energy Consumption Survey -1994
- a - Heat range values from *U.S. and Canadian Labor-Energy Survey 2000*, Portland Cement Association
- b - There are negligible secondary energy additions for waste fuels. The final tacit value is assumed to be the midpoint of reported heat values.
- c - Secondary energy requirements for electricity are based on the heat rate given in Table A.16 minus 3,412 Btu

Table A.15 - Carbon Equivalent Emission Coefficients for Fuels Associated with Cement Production

This table presents the carbon equivalent emission values for the fuels and materials associated with the production of cement. The carbon dioxide equivalent can be obtained by multiplying the carbon equivalent by (44/12), the mass ratio of carbon dioxide to carbon.

FUEL	Btu per Input Unit Tacit	Input Unit	Carbon Emission Coefficient *	Carbon Emission Coefficient Source	Percent Carbon (EGGUS)	API Gravity (EGGUS)	Density Pounds/gal (EGGUS)	Million Btu/bbl (EGGUS)
Mt/QBtu								
Coal	22,553,000	short ton	25.63	EGG2000		n/a		
Bituminous/Sub	22,340,000	short ton	25.81	EGGUS		n/a		
Petroleum Coke	30,120,000	short ton	27.85	EGG2000				
Green Coke	28,400,000	short ton	27.85	EGG2000	92.3	n/a	9.543	6.024
Calcined Coke	30,858,000	short ton	27.85	c				
Pitch	-	-	20.62	d	85.8	25.6		
Natural Gas	1,030,000,000	million ft3	14.47	EGG2000				
Fuel Oil, light (#2)	155,000	gallon	19.95	b	86.3	33.9	7.064	5.825
Fuel Oil, medium	144,000	gallon	20.72	a				
Residual Fuel Oil	154,690	gallon	21.29	EGG2000	85.7	17.0		6.287
Distillate Fuel Oil	143,690	gallon	19.95	EGG2000				
Lube Oil	149,405	gallon						
Gasoline	135,860	gallon	19.34	EGG2000	86.6	58.6		5.253
Kerosene	140,200	gallon	19.72	EGG2000	86.1	41.4		5.670
Diesel	140,200	gallon	19.95	EGGUS	86.3	35.5	7.064	5.825
LPG	85,790	gallon	16.99	EGG2000				
Propane	91,050	gallon	17.20	EGGUS				
WASTE -								
Oils	122,500	gallon	17.63	e				
Solvents	92,500	gallon	13.17	f				
Tires	28,500,000	ton	32.39	g				
Solids	-	-	20					
Misc.	-	-	20					
Electricity					lbsCO2/kWh			
Hydro Electric								
Average U.S. Electric			49.02		1.35 CDE			
Coal-Fired Electric			76.97		2.12 CDE			

* Mt/QBtu - million metric tons of carbon per Quadrillion Btu (10⁶ metric tons / 10¹⁵ Btu)

SOURCES

EGG2000 - Emission of Greenhouse Gases in the United States 2000, Energy Information Administration, U.S. DOE, Nov 2001, page 140
EGGUS - Emissions of Greenhouse Gases in the United States 1987-1992, Energy Information Administration, U.S. DOE, Oct 1994 Append
CDE - Carbon Dioxide Emissions from the generation of Electric Power in the United States, Oct 15, 1999, DOE & EPA
a - Medium Fuel Oil values are the average of the light and heavy fuel oil values
b - Diesel and light fuel oil is assumed to have the same carbon coefficient in EGGUS
c - Green coke and Calcined coke are assumed to have the same carbon coefficient.
d - Pitch is assumed to have the same carbon coefficient as asphalt reported in EGGUS
e - Waste fuel oils are assumed to have the same carbon coefficient as Medium Fuel Oil
f - Waste solvents are assumed to have the same carbon coefficient as gasoline reported in EGG2000
e - Waste fuel oils are assumed to have the same carbon coefficient as Coal reported in EGG2000

Table A.16 - Electric Generation Heat Rates

	U. S. Electricity Produced in 2001 ¹ billion kWh <i>a</i>	Units Consumed ² <i>b</i>	Heat Content <i>c</i>	10 ⁹ Btu Consumed <i>b x c</i>	Btu/kWh <i>a / (b x c)</i>
Coal	1,904.0	975.6 10 ⁶ short tons	20,511,000 Btu/ton ³	20,009,916	10,509
Petroleum		32.0 10 ⁶ bbl Distillate 163.2 10 ⁶ bbl Residual 1.4 10 ⁶ bbl Other Liquids 4 10 ⁶ short tons Coke	5,825,000 Btu/gal ³ 6,287,000 Btu/bbl ³ 5,670,000 Btu/bbl ⁵ 14,200 Btu/lb ⁶	186,517 1,025,837 7,932 118,116	
sub-Total	126.0			1,338,402	10,622
Natural Gas	613.0	5,690 10 ⁹ ft ³	1,019 Btu/ft ³ ³	5,798,110	9,459
Other gases	14.1	127 10 ¹² Btu		127,000	9,007
Nuclear	768.8	10,623 Btu/kWh ⁷		8,166,962	10,623
Hydroelectric	217.5	3,412 Btu/kWh ⁴		742,110	3,412
Renewable	79.8	808 10 ¹² Btu		808,000	10,125
Other	5.0	49 10 ¹² Btu		49,000	9,800
TOTAL	3,728.2			37,039,500	9,935

Source:

1 AER2001 - Annual Energy Review 2001. Table 8.2a Electricity Net Generation, page 224

2 AER2001 - Annual Energy Review 2001. Table 8.3a Consumption of Combustible Fuels for Electricity Generation, page 229

3 AEO2003- Annual Energy Outlook 2003, Energy Information Administration, U.S. DOE, Jan 2003 page 249

4 Convention based on assumed value used by EIA and others

5 assume diesel fuel is the majority of other fuels

6 Data from Mid-Continent Coal & Coke Co. for green petroleum coke

7 AER2000 - Annual Energy Review 2000. Table A.6 Nuclear Steam/Electric plants, page 336

APPENDIX B - Portland Cement Types and Their Use

The American Society for Testing and Materials (ASTM) Specification C-150 provides for eight types of portland cement. ASTM standards serve as the basis for manufacturing, procurement, and regulatory activities. More than 92% of portland cement produced in the United States is ASTM Type I and II (or Type I/II); Type III accounts for about 3.5% of cement production. Type IV and Type V account for less than 0.5% of production. Although IA, IIA, and IIIA (air-entraining cements) are available, concrete producers prefer to use an air-entraining admixtures during concrete manufacture, where they can get better control in obtaining the desired air content.

ASTM Type	Use
I ¹	General purpose cement, when there are no extenuating conditions. Widely used for concrete construction, including pavements, building foundations, bridges, floors, and various precast concrete products. Some ready mixed concrete producers add admixtures to meet specific job requirements.
II ²	Aids in providing moderate resistance to sulfate attack.
I-II	Meets the specification requirements for both Type I and Type II, the most widely used type for all kinds of concrete construction.
III	Used when high-early strength is required. It is chemically and physically similar to Type I, except that its particles have been ground finer. It is used when forms need to be stripped as soon as possible or when the structure must be put into service quickly.
IV ³	When a low heat of hydration is desired. (Used in massive structures.)
V ⁴	When high sulfate resistance is required. Type V gains strength more slowly than Type I cement and is used only in concrete exposed to severe sulfate action - principally where soils or groundwaters have a high sulfate content. This cement is particularly effective for structures such as sewage treatment plants and septic tanks.
IA ⁴	A type I cement containing an integral air-entraining agent.
IIA ⁴	A type II cement containing an integral air-entraining agent.
IIIA ⁴	A type III cement containing an integral air-entraining agent.

1 - Cements that simultaneously meet requirements of Type I and Type II are also widely available.

2 - Type II low alkali (total alkali as Na₂O < 0.6%) is often specified in regions where aggregates susceptible to alkali-silica reactivity are employed.

3 - Type IV cements are only available on special request.

4 - These cements are in limited production and not widely available.

APPENDIX C - Major Components of Cement

The chemical composition of cement influences the characteristics of cement and the concrete produced. The clinker mineral C3S is the majority clinker component. The strength developed by portland cement depends on its composition of C3S, C2S, C3A, C4AF and the fineness (Blaine) to which it is ground. The 'Standard Specifications for Portland Cement' contain different requirements of chemical and physical properties: MgO, SO₃, alkalis as Na₂O, ignition loss, insoluble residue, Bogue composition, fineness (Blaine), soundness, autoclave expansion, compressive strength and initial and final setting.

C3S - Tricalcium Silicate - Ca_3SiO_5 - $3\text{CaO}\cdot\text{SiO}_2$ - CAS #12168-85-3

C3S is the main clinker component in cement, typically more than 50 %

Quick development of strength - C3S reacts more quickly than C2S

High contribution to the final strength

Resistant to sulphur attack

25 weight % water bind under hydration of C3S

Heat development: 500 kJ/kg

Hydration of C3S ($\text{Ca}_3\text{SiO}_5 + (y+z)\text{H}_2\text{O} = z\text{CA}(\text{OH})_2 + \text{Ca}(3-z)\text{SiO}(5-z)y\text{H}_2\text{O}$) are to some extent dependent on the presence of C3A and gypsum. Both C3A and gypsum stimulate the hydration of C3S. Also Alkalis have some influence at the hydration.

$\text{C3S} = 4.071 \cdot \text{CaO} - (7.600 \cdot \text{SiO}_2 + 6.718 \cdot \text{Al}_2\text{O}_3 + 1.430 \cdot \text{Fe}_2\text{O}_3 + 2.852 \cdot \text{SO}_3)$
according to Bogue's methods

C2S - Dicalcium Silicate - Ca_2SiO_4 - $2\text{CaO}\cdot\text{SiO}_2$ - CAS #10034-77-2

C2S is the second clinker component in cement, between 10 - 60 %

Slow development of strength - C2S reacts more slow than C3S

High contribution to the final strength

Resistant to sulphur attack

20 weight % water bind under hydration of C2S

Heat development: 250 kJ/kg

On hydration, C2S shows similar behaviour to C3S, but is slower to react. It does however continue to hydrate late in the setting period, and may then contribute to the strength of the cement.

$\text{C2S} = 2.87 \cdot \text{SiO}_2 - 0.754 \cdot (\text{Ca}_3\text{SiO}_5)$ according to Bogue's methods

C3A - Tricalcium Aluminate - $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ - CAS #12042-78-3

C3A range in the cement between 3 - 10%

High contribution to the early strength

Low contribution to the final strength

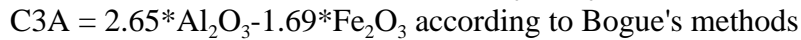
Not resistant to sulphur attack

40 - 210 weight % water bind under hydration of C3A

Fast and high heat development: 900 kJ/kg

Compared with C3S, C3A reacts very rapidly with water, giving two hydrated

products: $2C_3A + 21H = C_4AH_{13} + C_2AH_8$. These form platelets within the cement and convert to C_3AH_6 , which forms very quickly and is responsible for the initial formation of a crystalline network. In the presence of free lime in the cement, the formation of C_4AH_{13} is favoured. This slows the formation of C_3AH_6 , but even so the formation of C_4AH_{13} can cause the cement to set too quickly. To avoid speed setting, is gypsum added to the cement and the mineral ettringite is formed on hydration:



C4AF - Tetracalcium aluminoferrite - $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ - CAS #12068-35-8

C4AF Range in the cement between 5 - 10 %

Small contribution to the development of strength

37 - 70 weight % water bind under hydration of C4AF

Moderate to low heat development: 300 kJ/kg

Hydration of $C_4AF + 13H = C_4AFH_{13}$

$C_4AF = 3.04 \cdot Fe_2O_3$ according to Bogue's methods

Calcium Sulfate dihydrate (Gypsum) - $CaSO_4 \cdot 2H_2O$ - CAS #7778-18-9

Alkalis

($Na_2O + K_2O$) Cements with a low alkali content may be required for use in the manufacture of concrete, in which the use of aggregate introduces silica. Alkalis may enhance reactions with amorphous silica. The content of alkalis contributes to the acceleration of the early strength and lowering of the final strength. The content of alkalis is dependent on the raw materials but also the manufacturing process also determines the content of alkalis. Cement manufactured by the wet processing will contain less alkalis compared to dry processing.

Alkalis as $Na_2O = Na_2O + 0.658 \cdot K_2O$

Magnesia - MgO

Cements with a high magnesia content may hydrates and expand after setting.

Lime - CaO

Cements with a high free lime content may react with water and result in expansion.

Calcium Carbonate - $CaCO_3$ - CAS #1317-65-3